A PRACTICAL ELEMENTARY CHEMISTRY

D. W. McFARLAND

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BY

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A

PREFACE

FOR a good many years the author has been convinced that the conventional form of text-book on chemistry does not produce the desired results. Chemistry was first taught by the lecture demonstration method. A great step in advance was made when the laboratory method of experimentation was introduced. Text-books were then written with the theory interspersed through the descriptive matter, and a laboratory guide was written to accompany the text. This is the common practice to-day. The results are admittedly unsatisfactory. One only has to read examination papers in chemistry to appreciate that the efficiency of the methods is very low. This is a result of wrong methods of learning the facts and theories of the subject. Nothing is done thoroughly. Many gaps are left in the subject, resulting in a mass of disconnected facts, and the student acquires neither an exact knowledge of the principles involved, nor honest habits of work or thought in the study.

Many teachers to-day do not make use of a descriptive text at all. The author long ago gave up assigning fixed lessons from the descriptive text. The present system has been in use in the New Haven High School for about ten years, and the results certainly justify a careful examination of the methods which produce them. The present plan is built entirely upon an exhaustive study of the laboratory work, not as illustrating the statements made in the descriptive text, but as the foundation of the whole subject. It is built on the plan of developing fundamental classes of reactions in the laboratory designed to fix certain fundamental principles of chemistry in the minds of the pupils. In connection with this, the pupil is supposed to look up certain additional facts and theories in connection with the work, as those facts and theories seem to be needed or are called for in the recitation connected with the practical work. This results in the pupil's using the descriptive text as it should be used; that is, looking up

references as needed, and fitting the facts into a general outline previously decided upon. It at once makes the course elastic, and makes it easy for both the weak and the strong student to get all that they need for the work. According to this plan the weak student does his best, and gets full credit for it; the strong student may get five or ten times as much, and at once feels that the study is a dignified subject worthy of his best efforts.

The ideal condition in teaching chemistry would be one pupil and one teacher, without any text-book or laboratory guide whatever. Practical considerations, however, necessitate the handling of pupils in classes. Some sort of printed material at once becomes necessary. This course puts into the hands of the pupil a book which is almost as good as a private teacher at his side. Whenever a question occurs to him, he simply has to turn to the reference, and he finds just what the teacher would tell him on that particular point.

The Form of the Book

For seven or eight years now, in the author's classes, the pupil has been provided with a laboratory guide, not only containing all of the directions for the experiments, but also all of the explanations and theories necessary for an intelligent understanding of the chemical principles involved. A text-book has also been in his hands for reference concerning descriptive matter.

This book is simply what the author has been using, improved wherever an improvement seemed necessary. It consists of four parts.

Part I contains all of the laboratory directions, accompanied by questions involving a knowledge of principles. Not only are references given at the end of each of these questions, to some paragraph in another portion of the book, where more light is thrown on the matter, but these reference numbers are inserted at numerous points all through the directions.

This gives every honest pupil a chance not only to look up things for himself, but it develops the habit of looking up references on the subject, and making sure that he is posted on the facts before coming to any conclusions. The system, if carried out, develops the habit of looking through the theory and descriptive matter in the book many times, so that the pupil literally becomes familiar with the whole of the subject. It

has not been an uncommon experience for one of the pupils to learn everything in the course. This means, that he learned the subject as a whole and not as a collection of disconnected facts and theories difficult to remember. Each subject met in the laboratory is exhaustively studied as a whole, according to a specified form. The continuous process of looking up the desired facts and theories results in a vast amount of repetition of fundamental ideas, and these become fixed in the mind as a kind of second sense.

Part II. This part contains all the very elementary theory which it is absolutely necessary for a pupil to know in order that he may be able intelligently to study and remember the subject. Most of it is taught in class in connection with the laboratory work. It is in the early part of the course that the pupil learns the language of chemistry, and hence is able to remember the facts without apparent effort. The subject of symbols, formulas, and equations is gone into extensively, and their use and meaning becomes extremely simple. If symbols, formulas, and equations are to be referred to at all, it is necessary that they should be thoroughly understood. It is surprising how little trouble they cause when they are attacked energetically.

Part III. This has to do with what has been called the *more advanced theory*. It is not essential to the very elementary study of the subject, but is designed for those pupils who expect to go to college, or who expect to attain an advanced standing in the subject. At the same time, references to it are inserted all through the laboratory directions and descriptive text for the benefit of those pupils who are really interested and are not content to let things go without explanations. A mastery of this part in connection with the elementary course will enable a pupil to pass off the first-year work in chemistry in any college.

Part IV. As has been stated, the course in chemistry which has been in use in the New Haven High School for the past ten years was primarily based on the laboratory work. The theory was taught in class, the descriptive part being obtained from a text-book. The text-book does not always give all that the pupil would like to find. The author has long felt that the course would be much benefited if the existing laboratory guide were supplemented by a descriptive volume especially designed to go with it. This Part IV is an attempt at such a

descriptive part.   In it has been placed such matter as it seemed
to the author might reasonably be called for in reading up in
connection with the laboratory work.   In writing it the gen-
eral scheme for recitation has been followed.   It seems as
though this systematic treatment was very necessary.   All
new terms, processes, and paragraph headings are in black-
faced type.   All references are by paragraph number.   This
makes it possible to turn very quickly to the desired reference.

There are many repetitions in this part.   It should be re-
membered that it is to be used for reference, and not as the
ordinary text-book is used; therefore important ideas, which
experience has shown are sometimes not emphasized enough,
are repeated.

Practical applications.   All of the common practical appli-
cations of the ordinary chemical substances as well as chemical
processes are mentioned.   Any pupil who has mastered this
course will at once know of the possible practical applications,
without having been actually taught them.   The course is
elastic.   A teacher who wants to make a specialty of practical
applications of the subject will find ample material.   A teacher
preferring to dwell on the technical processes in manufacturing
will also find all that he needs.

The system.   This system of teaching chemistry has certainly
produced remarkable results.   It is not an experiment.   It has
been in use in the author's classes for over ten years.   It has
been in use in many other schools all over the country for the
past six or seven years.

The explanation of its success lies in the fact that the course
is based on an exhaustive study of the experiments themselves.
The theory is introduced little by little as needed every day.
The pleasant trip through the chemistry country is not ruined
by week-long barren wastes of theory, apparently having no
connection with the rest of the subject.   The pupil revels in
his ability to do the work and apparently enjoys it.   He learns
the scientific method of going at the work, that is, the common-
sense method.   Modern ideas of efficiency are involved in
every point in the course: *i. e.*, how to get the desired results in
the shortest time, with the least effort.

In conclusion, the author wishes to express his thanks to
Doctor P. T. Walden, Doctor H. W. Foote, and Doctor B. B.
Boltwood, of Yale University, for many valuable suggestions
and kindly criticisms.

SUGGESTIONS TO THE TEACHER

The following course in chemistry may be considered as being divided into four parts: Part I, the study of the language of chemistry; Part II, the study of the reactions of the non-metals, including oxidation in the "wet way"; Part III, the study of the reactions of the metals or of applied chemistry; and Part IV, a general review of the applications of the principles of chemistry.

The work begins in the laboratory with exercises requiring little or no recitation work. In the recitation periods accompanying the laboratory work, Part II of the book is taken up, and very intense drill is given on the meanings and uses of symbols, formulas, and equations. In addition to the first twelve laboratory exercises, the pupil is expected to master everything up to Article 105. Most of this is actually taught in class, very little assigned work being given. The pupil is required to express himself very exactly, and with a speed that assures the teacher at once of the pupil's absolute mastery of the subject.

Especial stress should be laid on the following topics:

1. Symbols and names of the common elements in groups.
2. Full meaning of the formula of a compound.
3. Combining powers or valences of the different elements.
4. Formulas of binary compounds.
5. How many grams of any one element would be chemically equivalent to ten grams of any other element.
6. Full meaning of a chemical equation.
7. Equations showing the formation of binary compounds from the elements.
8. Symbols and names of radicals.
9. Formulas and names of compounds of each of the basic radicals with each of the acid radicals.

10. Seven general methods for the preparation of salts.

11. Drill in writing equations showing the formation of any salt containing oxygen in seven different ways. This drill should be so thorough that the pupil is enabled to complete all seven equations in one and one-half minutes.

All of the above may be accomplished to the entire satisfaction of both teacher and pupil in thirty-six recitations.

As a result of the above drill the pupil becomes so familiar with the meaning and use of symbols, formulas, and equations that during the rest of the course he experiences no trouble whatever in recording, remembering, and explaining the chemical changes that come under his observation. This drill also leads to an almost unconscious knowledge of the general subject of chemical equivalence, which is of the utmost value.

The second part of the course lasts about twelve weeks. During this time the reactions of the non-metals are studied, both in the laboratory and the recitation-room. It is during this time that the subject of oxidation in the "wet way" is taken up first. The subject is introduced in connection with the halogens. The pupil is shown how to determine the oxidizing power of any oxidizing agent, and is expected to write equations showing the preparation of any of the halogens from a salt in the presence of sulphuric acid and any oxidizing agent.

The first recitation following a laboratory period should be largely instructive and explanatory. At the second recitation the pupil should be required to state in his own words the exact results of every experiment, to write equations for every chemical reaction that has come under his observation, and to give the exact and full meanings of each equation.

Having gone over all of the points in reference to the laboratory work, it is now possible for him to write a complete report on the exercise strictly according to the outline for recitation. This report goes into his note-book and constitutes the preparation for the next laboratory exercise at which it is due and is examined. This results in a thorough reading of the descriptive matter in the text. The important part of this article is that relating to the actual work he did, which must be written so fully and clearly that a third person could not only learn what was done, but could duplicate the work. This results in much repetition of certain ideas which are otherwise apt to be neglected.

In the third recitation the whole subject is reviewed and discussed. The methods of preparation, the applications of the substance in the domestic and technical arts and sciences, and the common methods for the recognition of the substance are thoroughly brought out.

In the last twelve weeks of the course the study of the metals is taken up. This is usually very easy for pupils who have mastered the earlier parts of the course, for many of the re-actions have already been met. The scheme of recitation is about the same as for the non-metals. In the case of those who are not going to college, in place of the study of all of the metals, the pupils take up, both in laboratory and recitation, common domestic applications of chemistry, making many examinations of common substances, examples of such work being given in the last part of the laboratory instructions.

The fourth part of the course consists of a systematic review introduced whenever the nature of the laboratory work allows of sufficient recitation time for the purpose. The review exer-cises indicated in Tables I, II, and III, beginning on page 223, are of especial value. The exercise indicated in Table I is of the greatest value in giving a review of the whole subject. In this exercise the pupil is expected to state the possible steps in words, and also to represent them by equations. It includes all of the fundamental classes of reactions of elementary chemistry.

In the review exercise indicated in Tables II and III, the pupil is expected to start with the natural elements and com-pounds indicated in Table II and state in words the steps necessary to form any of the indicated elements or compounds indicated in Table III, not only to state the processes in words but to represent them by equations. He is not allowed to make use of any reagent the formation of which he has not already shown from the natural elements or compounds. All processes used must be practical and not mere algebraic inven-tions. This drill means that the pupil must look up almost every point in question. It leads to great repetition in the indicated preparation of the common reagents of the laboratory, and fixes the subject in the mind as nothing else will fix it.

Examples are constantly introduced in connection with the recitation work, beginning at the very start of the subject with the simple ones involving weights only. The other four classes

of examples are introduced little by little, until at the end of the year the pupil can solve the most complicated ones, involving volumes of liquids, specific gravities and per cents, and the reduction of gas volumes.

The course has been known to produce the most remarkable results.

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PART II. FUNDAMENTAL IDEAS

PART III. MORE ADVANCED THEORY

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AA

A PRACTICAL ELEMENTARY CHEMISTRY

PART I

LABORATORY WORK

EQUIPMENT AND DIRECTIONS

Personal equipment. Each student should provide himself with an apron, towel, piece of cloth, sponge, and a piece of soap.

The apron may be made of denim, perfectly plain, with a fixed strap to go around the neck and a button strap around the waist. It should be long enough to reach within four inches of the floor.

Individual laboratory equipment. With the help of the illustrations on the opposite page the student should learn the names of the following things the first day in the laboratory, and familiarize himself with the places where they are kept:

½-lb. glass tubing.
1 funnel tube (A).
1 combustion spoon (B).
1 glass bend, 45 cm. long (C).
3 pieces of copper wire.
1 piece of rubber tubing.
1 file.
1 pair of forceps (D).
1 glass stirring-rod (E).
1 iron wire loop (F).
8 squares of glass.
3 rubber connectors.
1 porcelain mortar (G).
1 porcelain pestle (H).
3 No. 8, 2-hole rubber stoppers.
1 No. 3, 1-hole rubber stopper.

3 short right-angle bends, 8 cm. × 8 cm.
3 medium right-angle bends, 8 cm. × 15 cm.
1 No. 2 beaker (I).
1 3-in. porcelain evaporating dish (J).
1 8-oz. flask (K).
1 funnel (L).
6 150-c.c. wide-mouth bottles.
2 500-c.c. bottles.
1 test-tube rack (M).
12 test-tubes in rack (N).
1 test-tube holder (O).
1 bulb test-tube (P).

Equipment for general use.

1 water-pan (Q).
1 beehive shelf for pan (R).
1 lamp-stand, two rings, one clamp (S).
1 filter-flask with rubber tubing (T).
1 sieve funnel (U).
1 1000-c.c. wide-mouth bottle.
1 centimeter scale.
1 package filter-paper.
1 bundle splints, toothpicks.
Disks of filter-paper for porcelain funnel.
1 wire gauze with asbestos centre (V).
1 iron crucible (W).

1 iron plate, depression in centre, 2 in. square.
1 piece cobalt glass, 4 in. square.
1 thermometer.
1 package common wrapping-paper.
1 50-c.c. graduate or measuring glass (X).
8 reagent bottles.
1 litmus-paper bottle.
2 Bunsen burners with tubing (Y).
1 test-tube cleaner (Z).
1 incandescent lamp in series with terminals.
1 pinch-cock (AA).

For approximate prices, see 283–284.

Students are expected to keep their supply of apparatus complete. When things are lost or broken they should be replaced at once. It is impossible to do good work with an insufficient supply of apparatus.

CARE OF THE TABLE AND LOCKERS

Sponge off the table after every laboratory exercise with a moist sponge, whether anything has been spilled on it or not, and wipe it dry with a cloth.

Keep the reagent bottles in the proper order, viz., from left to right—sulphuric acid, concentrated, dilute; nitric acid, concentrated, dilute; hydrochloric acid, concentrated, dilute; ammonium hydroxide and sodium hydroxide.

Wash all the reagent bottles and sponge off the shelves once a week.

Keep all of your own apparatus clean and in the right place.

DON'T put the general apparatus in your private locker.

SOME LABORATORY DON'TS

Don't throw solids in the sink.
Don't boil sulphuric acid.
Don't pour water into hot sulphuric acid.

Don't aim a test-tube at your neighbor. Point it to the right, down the middle of the table.

Don't put **anything** into the reagent bottles, not even the reagent itself.

Don't mix chemicals on your own account. Students who are found doing this should be dismissed from the laboratory.

Don't use large quantities where small quantities will do just as well.

Don't depend entirely on your own observation for your facts; verify them by reading up the subject in the various reference books.

Don't pay any attention to the way your neighbor is doing his work.

REMEMBER

1. Neatness is of the first importance.

2. You will be marked on the way you keep your desk and locker.

3. To follow directions implicitly, but try to understand the reasons for them.

4. Every laboratory exercise is made up of many small experiments. Make sure that the object of each of these experiments is accomplished.

5. You are responsible for the results, whether you do the work or not.

6. You can learn what would have happened if you had done the work by reading the references in the descriptive text.

7. Always to take your laboratory note-book and text-book to all exercises, both recitations and laboratory work.

8. To keep all of your senses on the alert. Read the signs and ask questions about things you do not understand.

9. Learn the names of the common minerals and chemicals in the cases.

THE NOTE-BOOK

Every laboratory exercise should appear in the note-book in three parts, as follows:

Part I.   This part should contain notes on whatever the instructor has to say before class.   It theoretically contains the directions for the laboratory work, but where a printed laboratory guide is used it is only necessary to refer by number or page to the printed directions.   There are sure to be slight variations or additional directions which should appear in this part.

Part II.   This is the most important part of the book and is to contain all of the original notes on the laboratory work written by the student during the course of the experimental work.

The notes should be short, on separate lines, contain a brief reference to what was done, and be numbered and lettered to correspond with the directions.

Part III.   This part is invariably to consist of a report on the work done or that might have been done, written in the third person, past tense, passive voice.   If he did not finish the work, when he has written his report on what he did do the pupil should use the subjunctive mood and describe what would have happened if he had done the rest.

This report must be instructive and ready to print.   If it is not so written that a person ignorant of the subject could not only learn something from it but could duplicate the work, it is not satisfactory.   This writing up of the laboratory work is an extremely important part of the course.   It not only causes the student to review the work, but teaches him to write businesslike reports in good English on work done.

If the subject of the exercise is a substance, Part III should be a composition on that subject written according to the following outline, but containing an exact report on the experimental work as above.   It should be divided into paragraphs according to the topics covered, each paragraph heading being indented and underlined.

GENERAL OUTLINE TO BE FOLLOWED IN RECITATION AND IN
WRITING COMPOSITIONS

Appearance and state.   That is, is it a solid, liquid, or gas?
What color?

Occurrence in the free condition. Where and in what quantity?

Occurrence in the combined condition. Where and as what?

Physical properties. Can it be liquefied, solidified, or gasified, and under what conditions?

Will it dissolve in water or other liquids, and to what extent?

If it is a gas, how does its volume change with a change of temperature or pressure? Charles's and Boyle's laws? (155–157).

If it is a gas, what does a liter weigh at normal temperature and pressure? Weight of a liter is equal to 22.4 g. divided by the molecular weight of the gas.

If it is a solid or liquid, what is its specific gravity? (281).

Chemical properties. If it is a gas, will it burn or support combustion?

If it is a compound, can it be decomposed and how?

If it is an element, does it combine with oxygen?

What oxides does it form and are they basic or acidic? (96–103). Does it form any compounds with hydrogen?

What experiments might be done with it? Describe them in detail. Give all equations involved.

Test. The common test for it if it is an element, or for its two radicals if it is a compound.

Preparation. The common way it is made in the laboratory.

The common way it is manufactured.

Two other possible ways.

Give all equations showing the different methods of preparation.

Common compounds not already mentioned. The chemical name and formula. The common name and the mineral name.

Uses. In manufacturing, in the household, in medicine.

NOTE. It is not expected that answers will be found for every one of these questions for any one substance. Whatever facts are learned either from the laboratory work or from the descriptive text are to be fitted into the outline.

SPECIMEN EXERCISE

May 24.   Laboratory Exercise No. 49

Experiments with Red Oxide of Mercury

Part I.

1. Heat a small quantity of oxide of mercury in a sealed tube. Is a gas given off? Is it oxygen? What is left in the tube?
2. Will this oxide dissolve in the common dilute acids? In order to test this question add in separate test-tubes a very small quantity of the oxide to about an inch of the different acids. Heat if necessary.

Part II.

1. (a) Red oxide of mercury is a heavy red crystalline powder.
   (b) When heated in a sealed tube it first turns a dark color.
   (c) A rubber tube connected with the sealed tube and dipped in water shows by bubbles that a gas is being given off.
   (d) A spark on the end of a splint introduced into the tube during the heating bursts into flame, indicating that the gas is oxygen.
   (e) Something like a mirror forms on the inside of the tube just beyond the hot part.
   (f) After a time there is no more of the red powder left, but silver globules may be seen on the inside of the tube. This must be mercury.
   (g) On cooling, a red color appears on the mercury in the tube.
2. (a) The red oxide dissolves readily in cold dilute hydrochloric acid.
   (b) It also dissolves easily in cold dilute nitric acid.
   (c) It dissolves slightly in hot dilute sulphuric acid.
   (d) When much of the oxide is added to a small quantity of hydrochloric acid, heat is generated.
   (e) All of the above solutions were colorless.

Part III.   Red oxide of mercury is a heavy red crystalline powder. In the laboratory it is known as mercuric oxide. In the drug-store it is known as **red precipitate.** There is another form of mercuric oxide known in the drug-store as **yellow precipitate.** Both of these are used in certain ointments. There is a lower oxide of mercury known as mercurous oxide, which is black.

Heating mercuric oxide. A small quantity of the oxide was placed in a sealed tube and heated in the Bunsen flame. In order to test whether or not an invisible gas was given off, a

short piece of rubber tubing was connected with the end of the sealed tube and the other end of the rubber tube dipped into water. The appearance of bubbles during the heating indicated that such a gas was being evolved. The rubber tube was then removed and a spark on the end of a splint introduced. It promptly burst into flame with a slight explosion. This indicated that the gas was oxygen. In the meantime it was noticed that a silver-like substance was forming on the inside of the tube a little above the hot part. This was mercury. It is evident that the molecule of the red oxide was broken in two by the heat, the oxygen gas escaping and the mercury left in the tube. This may be represented by the following equation:

$$2 \text{ HgO heated} = 2 \text{ Hg} + O_2.$$
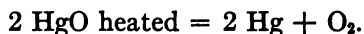
This equation shows that two molecules of mercuric oxide when heated give two molecules of mercury and one molecule of oxygen.

After a while there was no more red powder left in the tube. All had been decomposed. When the tube was allowed to cool and carefully examined it was found that the mercury in the tube was covered with a red coating. This was because when the temperature fell to the proper point some of the oxygen in the tube recombined with the mercury, forming the red oxide again. Here is an example of a reaction that goes both ways according to the temperature. Such reactions are said to be **reversible**.

$$2 \text{ Hg} + O_2 = 2 \text{ HgO}.$$
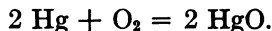
When it is desirable to represent a reversible reaction the double arrow is used, thus:

$$2 \text{ HgO heated} \rightleftarrows 2 \text{ Hg} + O_2.$$
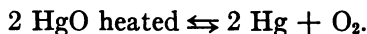
Solubility in acids. Mercuric oxide dissolves readily in cold dilute hydrochloric acid as well as in cold dilute nitric acid. Heat is set free in this reaction. The solutions are colorless. In the first case mercuric chloride (bichloride of mercury or corrosive sublimate) was formed together with water. The equation for this reaction is as follows:

$$\text{HgO} + 2 \text{ HCl} = \text{HgCl}_2 + H_2O.$$
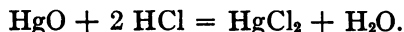
In the second case mercuric nitrate was formed with water. Equation:

$$HgO + 2\ HNO_3 = Hg(NO_3)_2 + H_2O.$$
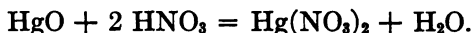
A similar reaction took place with dilute sulphuric acid, but the compound was not so readily soluble and some separated out on cooling. The compound was mercuric sulphate. Equation:

$$HgO + H_2SO_4 = HgSO_4 + H_2O.$$
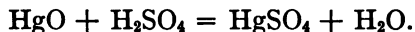
REMARK. The above illustration shows very well what is desired in the note-book work. It may not be possible to get the student to work out every exercise as thoroughly as the above, but it is possible to get him to take exact notes in Part II and to write some of them up thoroughly. The teacher should insist on exact scientific statements as far as the work is done. It will soon be found that many have formed the habit, and he can concentrate his attention on those who have either failed to get the idea or are trying to get along without any honest effort.

LABORATORY WORK

Abbreviations Used in the Directions

c.c., cubic centimeters.

g., grams.

s.q., small quantity. About enough to fill the curved part of the bottom of a test-tube.

t.t., test-tube.

ppt., precipitate.

conc., concentrated.

dil., dilute.

mm., millimeters.

cm., centimeters.

LABORATORY EXERCISE No. 1

Construction and Operation of the Bunsen Burner

1. Note the general construction of it (Fig. 1) (313). 2. Take it apart and make a drawing of each piece. 3. Four ways in

which, sooner or later, it will be found burning. 4. Which is the correct way? 5. How to correct it when it is found burning at the base. 6. Make a drawing of the Bunsen flame. Note two parts. 7. Push a pin through a match-stick $\frac{1}{4}$ in. below the head. Suspend the long end of the stick in the tube of the burner. See that the head is centred. Turn on the gas full and ignite it (311). 8. Place the lower end of a 4-in. tube in the lower centre of the flame. Ignite the gas issuing from the upper end. 9. Heat a strip of thin-sheet copper in the flame. What is the scale that collects on the outside? (751). Has it two colors? (749). What is the hottest part of the flame? Find the part that most readily melts copper wire. In general, what is formed when a metal is heated in the air or oxygen? (315).
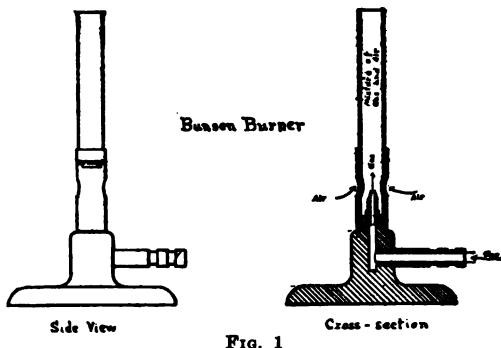
Bunsen Burner

Side View   Cross - section

FIG. 1

LABORATORY EXERCISE NO. 2

Working with Glass

Materials. Soft German glass tubing, 7 mm. diam., thick walled.

Apparatus. Triangular file.

1. **To cut glass tubing,** make a short sharp scratch across the tube with a file, place the file on the table directly under the scratch, with the scratch uppermost, then bear down gently on the tube in order to break it. If the scratch is properly made very little force will be necessary.

2. **To round the edges of a glass tube,** place the end in the hottest part of the flame (above the top of the inner cone), and rotate it slowly. Note the color of the flame. It is due to the sodium in the glass. Is there anything to be seen in the tube

during this process? (310). As soon as the flame has changed color the sharp edges have rounded.

3. **To seal the end of a tube,** hold in the hottest part of the flame until it has sealed itself, rotating it slowly. Tubes made in this way cannot be reheated without cracking (Fig. 2).

FIG. 2
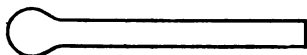
FIG. 3

FIG. 4

4. **To make a bulb tube,** seal the end of a tube as above, then remove it from the flame and blow carefully at once until the bulb is of the required size (Fig. 3). Why is it not well to blow while it is in the flame? Try it.

5. **Ordinarily, to make sealed tubes,** take a piece of tubing just twice as long as the sealed tubes desired. Soften in the middle. Remove from the flame and draw it out into a long thread. Break off the thread at the proper place and seal up the small hole (Fig. 4).

6. **To bend glass tubing,** heat it lengthwise in an ordinary gas flame until it is quite soft; then remove it from the flame and bend it quickly to the required curve (Fig. 5). **Do not attempt to bend it after the glass begins to harden.**

CORRECT BEND

INCORRECT BEND
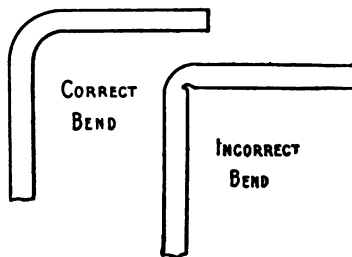
FIG. 5

7. Make thirty or forty sealed tubes as in 5. They will all be

FIG. 6

needed in the course of the work. Make a fountain-pen filler or medicine-dropper (Fig. 6). The rubber bulb may be obtained at the druggist's.
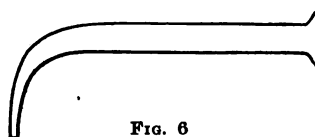
Questions on Exercise No. 2. Describe how to cut glass tubing. Why does the flame turn yellow? (625). Where does the water come from which collects in the tube when sealing the end? (310). When making a sealed tube, why is it undesirable to leave a great mass of glass on the end? Why cannot glass tubing be properly bent in a Bunsen flame?

LABORATORY EXERCISE No. 3

The Preparation and Some Properties of Oxygen. Acids and Alkalies

Materials. Oxygen mixture; magnesium; splints; magnesium oxide.

Apparatus. Water-pan; lamp-stand; test-tube; delivery-tube; bottles; forceps; glass plates.

Definitions. Acid (**63**); alkali (**65**); basic oxide (**67**); alkaline oxide (**68**); acidic oxide (**69**).

A **delivery-tube** is any combination of rubber or glass tubing by means of which a gas may be transferred from one place to another.

The collection of gases should be demonstrated by the teacher.

1. Fit a test-tube with a rubber stopper and delivery-tube. Fill the tube about an inch deep with the oxygen mixture. Fix the tube in the clamp of the lamp-stand, in a nearly horizontal position, as in Fig. 7. The mouth of the tube should be a little lower than the heated portion. Jar the tube so the mixture will lie as shown. Apply the Bunsen flame, holding the burner in the hand, being careful not to

FIG. 7

melt the tube. Collect the gas in bottles in the water-pan. Have all bottles filled with water and inverted in the pan. Cover the bottles with glass plates before removing from the water. Fill several bottles with the gas and generate more if necessary (**301**).
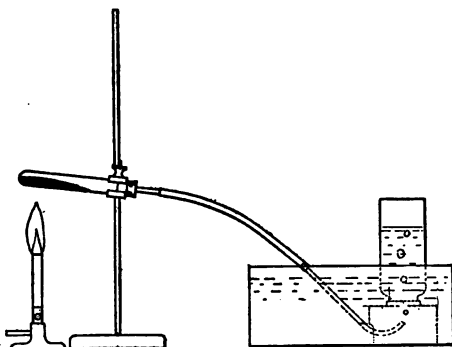
2. Thrust a splint with a spark on the end into a bottle of oxygen (**299**).

3. Holding some magnesium wire in the forceps, ignite it and plunge it into another bottle of oxygen (310). Burn several pieces in the same bottle. What is the product formed? (50). Add a small quantity of water to the bottle and shake it well, then drop in some litmus paper, both colors (705).

4. Test the solubility of magnesium oxide in water and dilute acids. In which does it dissolve most readily? (705). Is it a basic or acidic oxide? (97).

5. Make very dilute solutions of each of the acids and alkalies on the shelf, in test-tubes, using not more than one drop of each to a test-tube full of water. Test each solution with litmus paper. Which react acid and which alkaline? (63, 65).

Never lay the stopper of a bottle down on the table. Turn the hand over, take the stopper between the first and second fingers, remove it from the bottle, pick up and use the bottle with the same hand, then replace the stopper.

Questions on Exercise No. 3. Define the terms, acid (63); alkali (65); basic oxide (67); alkaline oxide (68); and acidic oxide (69). How did you prepare oxygen? (301). What is the effect of thrusting a spark into a bottle of oxygen? (310). If the wood contains carbon and hydrogen, what products would be formed? (310). What is the product formed when magnesium is burned in oxygen? (310). How does this moist product affect litmus paper? (68). Is it a basic or acidic oxide? (68). In what will basic oxides generally dissolve? (67). In what respects are all acids alike? (63). How would litmus paper be affected by vinegar, soap, washing-powder, lemon-juice, sour milk? Take some home and test it.

Laboratory Exercise No. 4

Some Properties of Metallic Oxides

Materials. Sodium wire, made before the class, or bits of sodium cut before the class; mercuric oxide, HgO; splints; manganese dioxide, MnO_2; red oxide of lead, Pb_3O_4; calcium oxide, CaO; magnesium oxide, MgO.

Apparatus. Iron crucible; lamp-stand; funnel; filter-paper; stirring-rod.

Definitions. Properties of matter (8).

      Filtrate. The liquid which runs through a filter.

      Residue. The material left on the filter.

NOTE. A solution is always transparent. If a liquid is not transparent it probably contains a finely divided solid that remains in suspension and could be filtered off.

How to use the lamp-stand.
How to make a filter.   To be demonstrated by the
How to filter.   instructor.
Use of stirring-rod.

1. Place a small piece of sodium on a piece of wet filter-paper. Turn up the edges of the paper so the melted sodium cannot roll off. The white smoke is sodium oxide (629).

2. Heat a piece of sodium wire in iron crucible on lamp-stand until no further change takes place. Let it cool for half a minute, add water, heat to boiling, and filter into test-tube. Feel the filtrate with the fingers and note its action on litmus paper (65). What is an alkaline oxide? (68).

3. Place a small quantity of mercuric oxide in a sealed tube, heat, and test the escaping gas with a spark on the end of a splint. What is left in the tube? (737).

4. Heat manganese dioxide in sealed tube, and test escaping gas for oxygen (774).

5. Repeat, using red lead (613).

6. Test the solubility of each of the oxides mentioned at the beginning of this exercise, in the dilute acids, and tabulate the result (67). Caution. Use about an inch of each dilute acid at each trial and put in it a very minute quantity of the oxide. Shake well and heat a little if the solution does not take place at once.

7. Which are alkaline oxides? (68). Which are basic oxides? (67).

Questions on Exercise No. 4. Define the term "properties of matter" (8). What topics should be considered when describing the properties of a given kind of matter? See outline for recitation (288). Describe some properties of sodium. Describe the visible effects of putting sodium on wet filter-paper (624). Is sodium oxide a basic or acidic oxide? (68). What would be formed if it were dissolved in water? (624). What is the effect of heating mercuric oxide? What gas comes out of the tube? What is left in the tube? What is left in the tube after heating manganese dioxide? What is the effect of heating red oxide of lead? (613). What kinds of oxides dissolve readily in acids? (68). How may iron-rust be removed from cloth?

LABORATORY EXERCISE No. 5

Preparation and Properties of Oxygen and Oxides of Non-metals

Materials. Manganese dioxide, MnO_2; oxygen mixture ($\frac{1}{2}$ MnO_2 and $\frac{1}{2}$ $KClO_3$); potassium chlorate, $KClO_3$; charcoal, C; sulphur, S; phosphorus, P; arsenic trioxide, As_2O_3.

Apparatus. Water-pan; lamp-stand; bottles; combustion spoon; iron plate; delivery-tube; forceps.

Definitions. Acidic oxide (**69**); acid anhydride (**70**); catalytic agent (**329**).

1. Generate oxygen as in 1, Laboratory Exercise No. 3. Collect several bottles of the gas. Generate some oxygen also by heating a few grams of potassium chlorate in a test-tube fitted with a rubber stopper and delivery-tube. Note the high temperature it requires to drive out the oxygen compared to that with the oxygen mixture. What does the manganese dioxide do in the mixture? (**329**).

2. Balance a small piece of charcoal on the combustion spoon, ignite it and lower it into a bottle of oxygen (**513**). When it will burn no longer add a small quantity of water to the bottle, cover it with the palm of the hand tightly, and shake the water about in the bottle (**70**). What kind of oxides do most non-metals form? (**67**). Test this water with litmus (**519**).

3. Pick up a small bead of phosphorus with the forceps and dry it by touching it to filter-paper. Place it in the cold dry combustion spoon. Ignite it in the hood and lower it in a bottle of oxygen carried there for the purpose. What is the white smoke? (**470**). What becomes of it? Add water to the bottle, shake, and test with litmus paper (**475**).

4. Ignite some sulphur in combustion spoon and lower it into a bottle of oxygen (**388**). Add water and shake (**402**). Test the water with litmus paper.

5. Place a dry piece of phosphorus on a dry iron plate; ignite it and cover it at once with a large dry bottle. Let it stand until the fumes have settled. These fumes are phosphorus pentoxide. Scrape some of the oxide out on a piece of

glass. Breathe on it. Add one drop of water to it. Test the product with litmus paper (475).

6. Test arsenic trioxide with litmus paper. See if it will dissolve in an alkali. What kind of an oxide is it? (484).

Questions on Exercise No. 5. Why is a mixture of manganese dioxide and potassium chlorate used for preparing oxygen? (301). What is left in the tube after no more oxygen can be obtained? How could you prove this? Why does the oxygen look smoky? What compound is supposed to be formed when carbon dioxide dissolves in water? (515). What kind of an oxide is CO_2, acidic or basic? (69). What two oxides does phosphorus form? (470). Under what conditions would each result? What acids would they form with water? What oxides does sulphur form? (388). What acids would these oxides form with water? (101). What gases would burn in oxygen? Would oxygen burn in any gas? (299). What acidic oxides must be given off when a match is ignited?

<div align="center">

LABORATORY EXERCISE No. 6

Preparation and Properties of Hydrogen

</div>

Materials. Mossy zinc; splints.

Apparatus. Lamp-stand; bottles; funnel-tube; 2 two-hole No. 8 rubber stoppers; test-tubes; one-hole rubber stopper; glass bends; rubber connector; water-pan; glass plates.

1. Hydrogen does not occur free (317). It must be obtained from some of its compounds. How may it be obtained from water? (330). In the laboratory it is most readily obtained from acids by the action of some metal (322). Zinc, magnesium, or iron acting on sulphuric or hydrochloric acid would produce the gas. Zinc and dilute sulphuric acid are commonly used.

FIG. 8

2. Set up an apparatus exactly as indicated in Fig. 8. The funnel-tube is passed through the ring of the lamp-stand simply to prevent the apparatus from being knocked over. It
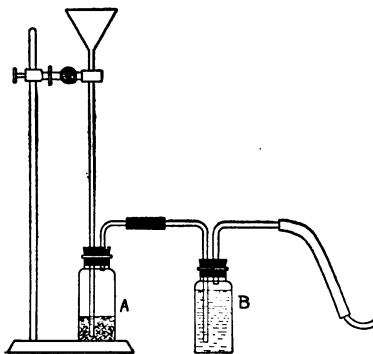
goes to the bottom of the bottle *A*, which is one-third filled
with mossy zinc.   A short bend comes from the other hole in
the stopper of this bottle and by means of a rubber connector is
joined to a medium bend which passes through another two-
hole rubber stopper and goes to the bottom of another bottle,
B.   This bottle is filled three-fourths full of water.   The de-
livery-tube is connected to the other hole in the stopper of this
bottle.   Enough water is now poured through the funnel-tube
to cover the zinc.   The water-pan is arranged to collect the
gas.   When the water is poured in, it displaces an equal volume
of air which should be allowed to escape.

3. Concentrated sulphuric acid is now added very cautiously
through the funnel-tube until the desired rate of flow of the gas
is obtained.

Sometimes the zinc and acid are too pure to react properly,
in which case the reaction will start readily if a little copper sul-
phate solution be added.   Collect all the gas that comes over,
keeping the bottles inverted and covered with glass plates.
The first bottles must contain a mixture of air and hydrogen.
Test the gas in the first bottles by applying the mouth of the
bottle to the flame.   If there is air present there will be a
peculiar explosion.   When the gas continues to burn quietly
in the bottle it is a sign that all of the air has been driven out
of the apparatus.   Does hydrogen burn?   What was formed
on the inside of bottles?

4. When the above precautions have been taken it is safe to
ignite the hydrogen on the end of the delivery-tube.   What is
the color of the flame at first?   Why does it become yellow in
a few moments? (625).

5. Does hydrogen support combustion?   In order to settle
this question place a 500-c.c. bottle of hydrogen, still covered
and inverted on a ring of the lamp-stand.   Twist a piece of
copper wire about the end of a splint.   Light the splint.   Hold-
ing the burning splint in the right hand near the mouth of the
inverted bottle of hydrogen, take the bottle in the left hand
and instantly thrust the blazing splint well up into the gas.
Leave it there a few seconds and withdraw it very slowly.
Does the gas support combustion? (320).

6. Is hydrogen lighter than air? (*a*) Leave one bottle of hydrogen standing upright with the cover off for one minute and another inverted with the cover removed for the same time. Then apply the mouth of each bottle to the flame. What do the results show? (*b*) Place an empty bottle, inverted mouth to mouth, over an upright bottle filled with hydrogen. Allow them to remain so for three minutes. Apply the mouth of each bottle to the flame. What does this show? (*c*) Obtain a clay pipe. Connect it to the delivery-tube and blow soap-bubbles with hydrogen. If a more rapid flow of the gas is desired, add a little more acid through the funnel-tube.

7. What is formed when hydrogen burns? Always, before igniting the jet of hydrogen, collect some of it in a test-tube and ignite it to see if it is explosive. It is a good plan to ignite the jet only by means of the burning hydrogen in the test-tube. When this can be done the gas coming from the generator has no air in it. Ignite the jet as suggested and place the burning hydrogen in a dry bottle. What is the vapor that condenses on the inside of the bottle? (331).

8. At the end of the exercise filter some of the liquid remaining in the generating bottle into a beaker or evaporating-dish and set aside until the next laboratory exercise. What is found in the dish? (712).

Questions on Exercise No. 6. How was hydrogen prepared in the laboratory? What other substances might be used? What acid will not give hydrogen with metals? (459). Why should the bottles be inverted? What is the color of the hydrogen flame? What would be the color if it were burning from the end of a glass tube? What is the most explosive mixture of hydrogen and air? Why is it dangerous to ignite the hydrogen coming from the delivery-tube at the beginning of the experiment? The bottle *B*, Fig. 8, acts not only as a wash-bottle but prevents the possible explosion of the generator itself. The most that can happen in this experiment is to blow the stopper out of the wash-bottle *B*. Why was water put in the apparatus? It is necessary to dissolve the zinc sulphate that is formed. The action may stop for three reasons. The zinc may be all dissolved, the water saturated with the zinc sulphate, or the acid may be exhausted. State three ways in which this gas might be obtained from water (330). State two ways in which it might be obtained from acids (322). What is the other product formed when sulphuric acid acts on zinc? (76). Describe three different experiments proving hydrogen is lighter than air. Mention one use of this gas (323).

LABORATORY EXERCISE NO. 7

Weight of Hydrogen Equivalent to 24 Grams of Magnesium

Materials.   Magnesium wire.

Apparatus.   Lamp-stand; No. 8 two-hole rubber stopper; funnel; soft-rubber tubing; pinch-cock; glass bend; delivery-tube; 2 150-c.c. bottles; water-pan; balance.

1. Arrange an apparatus as indicated in Fig. 9.   The funnel is passed through the small ring of the lamp-stand.   A piece of soft-rubber tubing is connected to the end of the funnel.   This is passed through a pinch-cock and connected with a straight piece of glass tube which goes through the rubber stopper to the bottom of the 150-c.c. bottle A.   A delivery-tube is connected with the other hole of the stopper, care being taken that it does not protrude through the stopper into the bottle. .

FIG. 9

2. Weigh exactly on a delicate balance from .1 to .15 g. of clean magnesium wire.   To avoid the necessity of this weighing the teacher may determine the weight of 1 cm. of the wire and have the student measure off the proper length, in centimeters, obtaining the weight by multiplying the weight of 1 cm. by the length taken.   This wire is placed in the bottle A.   The whole apparatus is then filled with water through the funnel-tube, care being taken that no air enters the tube.   The receiving-bottle D is then completely filled with water and inverted over the end of delivery-tube.   Concentrated hydrochloric acid is then run in through the funnel, the flow being controlled by the pinch-cock B so that **no air enters the tube.**   The action will begin at once and the evolved hydrogen caught in the bottle D.   When the action is over, a glass plate is placed over the mouth of the receiving-bottle

while the water both inside and out is at the same level.   The
bottle is then quickly removed from the water-pan, allowing
none of the remaining water to escape.   Remove the cover,
dry the bottle on the outside, and weigh both bottle and water.
Fill the bottle with water and weigh again.   The difference
between these two weights in grams will be the number of
cubic centimeters of hydrogen obtained.

3. Reduce this volume to the corresponding volume at **normal
temperature and pressure (254)**, as follows:

$$\text{Reduced volume} = V \times \frac{P - p}{760} \times \frac{273}{273 + t}.$$

in which formula V is the observed volume in centimeters, P the
observed barometric pressure in millimeters, p the correction for
the vapor pressure of water at the temperature t, in millimeters.

The barometric pressure should be read in millimeters, as
well as the correction for vapor pressure, the latter being taken
for the temperature of the water in the water-pan.   The final
result is the equivalent volume of hydrogen obtained at normal
temperature and pressure.   Multiply this result by the weight of
1 c.c. of hydrogen at normal temperature and pressure, which is
.00009 g.   Since a definite weight of magnesium produced this
quantity of H, how much would have been produced by 24 g.
of the metal?   The result should come out very nearly 2 g.

Questions on Exercise No. 7.   .144 g. of magnesium produced 140 c.c.
of hydrogen at a temperature of 17° C. and a pressure of 780 mm.   The
correction for vapor pressure of water was 14 mm.   What weight of
hydrogen would be equivalent to 24 g. of magnesium?

LABORATORY EXERCISE No. 8

Electrolysis (202)

Materials.   Sodium chloride, NaCl; potassium sulphate, K_2SO_4;
   litmus solution.
Apparatus.   Voltameter or electrodes and test-tubes; distilled
   water; beaker; source of electric current, 110-volt direct
   current through lamp.

Definitions.   Electrolysis. The process of decomposing a dis-
solved or melted substance by means of the electric cur-
rent.

Electrolyte. A substance which, when dissolved or
melted, will allow the passage of the electric current.

Electrodes. The terminals immersed in a liquid by
means of which the current enters and leaves.

Positive electrode. The one on which the oxygen ap-
pears.

Negative electrode. The one toward which the current
travels and on which the hydrogen or metals appear.

1. Will distilled water allow the current to pass through it?
Clean the voltameter by allowing water to run through it and
fill with distilled water. Turn on the current. Examine to
see if any bubbles appear on the electrodes. If no voltameter
is at hand the electrodes may be immersed in a beaker of water.

2. Repeat with hydrant water. Note that in each of these
cases very little current passes, but that more goes through in
the case of the hydrant water than in the case of the distilled
water.

3. Make a mixture of 100 c.c. of water and 5 c.c. of conc.
sulphuric acid. Place this in the apparatus and compare the
conductivity with that of water alone. If you have a voltam-
eter fill it with the above mixture and note the time neces-
sary to produce a definite volume of
hydrogen.
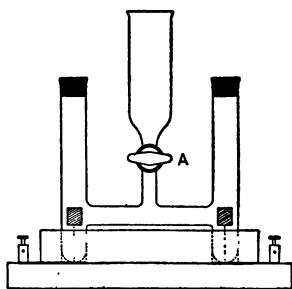
Fig. 10

4. If you have an apparatus simi-
lar to that shown in Fig. 10, fill it
with the above mixture through the
centre tube. Open the stop-cock at
A until the side tubes are just filled.
Insert rubber stoppers in each side
tube. Open the cock at A and turn
on the current. It will be noticed
that gas accumulates twice as fast in
one side as it does in the other. When one tube is filled turn
off the current, close the cock at A, and apply a light to the side
having the largest volume. What gas is it? Replace the rub-

ber stopper and insert a spark on the end of a splint in the other tube. What gas is it?

5. In similar manner test the conductivity of a strong solution of sodium hydroxide. What gases are given off? (203).

6. Make a solution of potassium sulphate and color it strongly with litmus solution. Clean the apparatus thoroughly and fill with this solution. Turn on the current. Explain the result (203).

Questions on Exercise No. 8. What is meant by electrolysis? What is an electrolyte? What are some common electrolytes? (193). Which is the positive electrode? Which is the negative electrode? Will distilled water allow the current to pass? Why does a small amount of current pass through hydrant water? Does hydrant water contain any dissolved solids? What effect has a small quantity of acid, base or salt on the conductivity of distilled water? What are the visible effects of passing the current through a solution of a salt colored with litmus solution? With the help of a piece of litmus paper moistened with salt water, how could you tell the direction of the current? What is an ion? (191). What relation does an ion bear to a radical? Toward which electrode does a positive ion travel?

LABORATORY EXERCISE No. 9

The Reduction of Metallic Oxides and the Preparation and Purification of Water

Materials. Copper scale, a mixture of cupric oxide, CuO, and cuprous oxide, Cu_2O; lead oxide, or **litharge**, PbO; potassium permanganate solution, $KMnO_4$; crystallized copper sulphate, $CuSO_4 + 5 H_2O$, known also as **blue vitriol**; copper gauze, 100-mesh; oxygen mixture.

Apparatus. Lamp-stand; wire gauze; flask; No. 8 two-hole rubber stopper; delivery-tube; funnel; filter-paper; sealed tubes; combustion spoon.

Definitions. Reduction (147). Reducing agent (148).

A **precipitate** is a solid that separates from solution. In the laboratory it is commonly formed by mixing two transparent solutions. When this is done, if the mixture is not **perfectly transparent** a precipitate has been formed.

Crystalline. A substance is said to be **crystalline** when it possesses naturally formed faces that reflect light.

Amorphous. Not crystalline.

Water of crystallization. Many substances when crystallizing from a water solution combine chemically with a definite number of molecules of water. This water is necessary for the crystalline form and color of the substance, *e. g.*, copper sulphate, or blue vitriol, $CuSO_4 + 5\ H_2O$ (**327**).

Efflorescence. Many substances containing water of crystallization give up part or all of this water to the air when exposed, thereby losing their crystalline form and color, and become amorphous powders. Such substances are said to **effloresce.**

Distillation. The process of boiling a liquid and condensing the vapor.

Distillate. The liquid that comes out of a condenser.

1. Hydrogen has a very great attraction for oxygen. It will not only combine with it directly, but it will extract it from other compounds and combine with it to form water (**335**). If a metallic oxide be heated in a stream of hydrogen the oxygen of the oxide will combine with the hydrogen to form water, leaving the metal in the free condition:

$$Cu_2O + H_2 = 2\ Cu + H_2O.$$
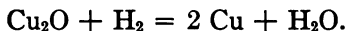
2. Push a small piece of copper-wire gauze, by means of the handle of the combustion spoon, a little more than half-way through a glass tube about 18 cm. long. Add to this half an inch of copper scale and push in another piece of gauze nearly to the oxide. Fasten the tube on the ring of the lamp-stand with copper wire in a horizontal position.

3. Place about 2 in. of mossy zinc in test-tube, cover with water and add half as much dilute sulphuric acid. Connect this with upper end of glass tube. When the whole apparatus is filled with hydrogen ignite the gas at the other end of the tube. Then heat the oxide with the flame. Note the water that appears in the lower end of the tube, and also the fact that the black oxide has changed to copper.

The same experiment may be performed, making use of illuminating gas in place of hydrogen. The illuminating gas

contains much hydrogen and will also show the formation of water.

4. Repeat exactly, making use of lead oxide in place of copper oxide. In this case it is necessary to see that there is a passage above the oxide for the gas to get through.

5. Water may be freed from suspended and insoluble matter by filtration. Dissolve some oxygen mixture in water in a test-tube and filter into another test-tube. What remains on the filter? What passes into the filtrate? Evaporate the filtrate to dryness in the evaporating-dish on wire gauze over the Bunsen burner. What is left in the dish? (338).

6. Water may be purified from all kinds of matter by distillation. Fill the flask half full of water. Add some sulphuric acid and potassium permanganate solution to render it impure. Arrange this on the wire gauze on the lamp-stand with a long glass delivery-tube, as shown in Fig. 11. Heat to boiling and collect some of the water that distils over. Note that it is neither acid in taste nor colored. It will have a slight odor of sulphur from the rubber stopper (338).
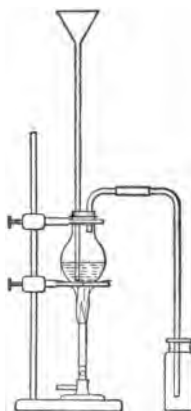
Fig. 11

7. Heat a small quantity of blue vitriol in a sealed tube. Where does the water come from? After the tube is cold, allow some of the water to run back on the anhydrous copper sulphate (174).

8. Hydrogen in combination will combine with oxygen in combination under certain circumstances:

$$Cu_2O + 2\,HCl = 2\,CuCl + H_2O.$$
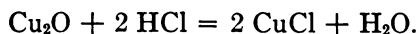
Dissolve a small quantity of copper scale in boiling dilute hydrochloric acid. Pour some of the solution into a bottle of water. It is impossible to see the water that is formed, but the heavy white precipitate is the copper chloride.

Questions on Exercise No. 9. What is meant by reduction? (147). What is a reducing agent? (148). What is a precipitate? How did you obtain a precipitate in this exercise? When is a substance said to be

crystalline? Name a crystalline substance. Mention an amorphous substance. What is water of crystallization? (174). What is efflorescence? (175). What is distillation and what is the distillate? What is the effect of heating a metallic oxide in an atmosphere of hydrogen? (335). What class of impurities does filtration remove from water? (338). How may water be freed from dissolved solids? (338).

LABORATORY EXERCISE No. 10

Solution and Crystallization

Materials. Sodium sulphate, $Na_2SO_4 + 10\ H_2O$; copper sulphate, $CuSO_4 + 5\ H_2O$.

Apparatus. Test-tubes; funnel; filter-paper; stirring-rod; mortar.

Definitions. A **cold saturated solution** is one containing all of a given substance dissolved in it which it can absorb at that temperature. It can be made in two ways: either by shaking an excess of the powdered substance with the liquid until no more will dissolve and filtering off the excess, or by cooling a hot solution and filtering off the substance that is deposited as a result of the cooling (167).

A **hot saturated solution** is one containing all of a given substance which it can dissolve at that temperature. It is best made by gradually adding the powdered substance to the boiling liquid until there is a decided excess present.

A **supersaturated solution.** When a hot saturated solution is allowed to cool, some of the material in solution generally crystallizes out. The amount that separates is the exact amount that the hot liquid dissolves more than the cold. Sometimes the excess refuses to crystallize when the hot saturated solution is cooled. The solution is then said to be **supersaturated** (168).

A supersaturated solution may be caused to crystallize either by dropping in a small crystal of the same material or by scratching the inside of the vessel with a glass rod.

Mother liquor. The liquid that is left after the crystals that have separated from it have been removed.

Decant. To pour off a liquid gently so as not to disturb the sediment.

Filter-flask. The filter-flask is an arrangement for rapidly filtering off crystals or solid residues by means of suction (Fig. 12). Fit the rubber stopper with the porcelain sieve funnel tightly into the flask, connect the rubber tube to the suction-pump, and turn on the water. Test the apparatus by putting the palm of the hand firmly down over the funnel; a decided suction should be felt almost at once. Moisten a small disk of filter-paper and fit it carefully over the sieve-plate. Shake up the material to be filtered and decant it quickly

FIG. 12

into the funnel. It will be sucked dry almost at once. If necessary and the substance admits of it, it may be washed free from the mother liquor by pouring successive small portions of water on it. The disk of filter-paper with the substance is then removed, placed on a larger piece of filter-paper, and set aside to dry.
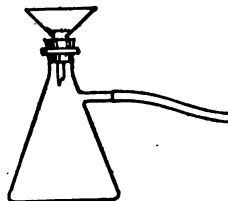
Preparation of a Supersaturated Solution of Sodium Sulphate

1. Wash 5 t.t. thoroughly; also the funnel. Prepare a filter and stand in it one of the tubes. See that no water remains in any of the tubes.

2. Place about 50 c.c. of water in the flask and heat to boiling on wire gauze. Stop the boiling and add 1½ t.t. full of sodium sulphate to the hot water. Shake the mixture for about three minutes. This will form a warm saturated solution.

3. Filter small portions into the several test-tubes, being careful that no drops touch the side of the tube. Cover each tube with a clean wet glass plate. Cool the tubes by standing in water or by letting water run over them.

4. If no crystals form during the cooling you have succeeded in obtaining supersaturated solutions. Into one tube drop a small crystal of the original salt. Scratch the inside of a second with a glass stirring-rod. Allow some dust from the floor to fall into a third. Simply shake a fourth thoroughly.

5. The crystals which separate contain 10 molecules of water of crystallization and are known as **Glauber's salt.**

6. Filter off this material by shaking the tube thoroughly and pouring the whole into the suction filter on the filter-flask. Set the product by until the next laboratory exercise and explain what has happened to it.

Preparation of a Supersaturated Solution of Copper Sulphate

7. Pulverize about 20 g. of copper sulphate, and add it little by little to a test-tube half full of boiling water until no more will dissolve. Filter into several test-tubes as before. On cooling, the salt will either crystallize out or will form a supersaturated solution. Crystallize as before. If crystals do not form, set the tubes aside until the next exercise. Examine under the microscope a drop of the blue liquid containing some of the minute crystals.

Questions on Exercise No. 10. What is a cold saturated solution? How is it made? What is a hot saturated solution? a supersaturated solution? How are such solutions made? How may a supersaturated solution be caused to crystallize? What is water of crystallization? What is the complete formula of Glauber's salt? What is the complete formula of blue vitriol? What happens to Glauber's salt if it is exposed to the air? (**175**). What happens to blue vitriol if it be heated? (**752**).

LABORATORY EXERCISE No. 11

The Action of Acids on Metals and on Basic Oxides (76–79)

Materials. Iron wire or thin wire nails; magnesium wire; zinc oxide, ZnO; magnesium oxide, MgO.

Apparatus. Lamp-stand; test-tubes; funnel; filter-paper; stirring-rod; beaker.

Definitions. Acid (63). Base (64). Salt (66). Basic oxide (67).

1. Fit a bulb test-tube with a rubber stopper and delivery-tube. Place about 5 g. of fine iron wire or 20 g. of thin wire nails in the tube. Fill the tube half full of conc. HCl. Fasten the tube in the clamp of the lamp-stand at an angle of about 45°, so the bottom of the tube will come near the base of the flame, as shown in Fig. 13. Place the flame near enough so the liquid will not boil over, but not near enough to cause it to evaporate. Keep the reaction going for about twenty minutes. Collect some of the gas over water and prove that it is hydrogen. All

iron contains sulphur and phosphorus.   These elements unite
with the hydrogen, forming the compounds H_2S and PH_3, each
of which possesses a disagree-
able odor and comes out of
the apparatus with the hydro-
gen. If not collecting the gas,
ignite it to destroy the odor.

2. At the end of twenty
minutes, or when the action
is nearly over, filter the liquid
into a test-tube. The filtrate
should be a deep green. If
it does not crystallize on
cooling, add an equal bulk of
conc. HCl. Examine under
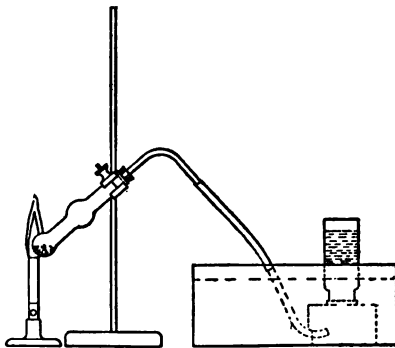
FIG. 13

the microscope a drop of the liquid, containing minute crystals.
The product is **ferrous chloride**, $FeCl_2 + 4 H_2O$ (**790**).

3. To about 3 c.c. of dil. sulphuric acid in evaporating-dish
add bits of magnesium wire until there is no further action. The
spray from this is very disagreeable, so the reaction had best
be carried out in the hood.   After cooling notice the formation
of crystals of salt.   The crystals contain seven molecules of
water of crystallization and are known as **Epsom salt** (**708**).

4. Make ferrous sulphate just as you made ferrous chloride,
but in place of concentrated acid use dilute sulphuric acid
with an equal bulk of water.   The product is known as **green
vitriol** and has the formula $FeSO_4 + 7 H_2O$ (**796**).

5. Write in Part III, after the description of the work,
twenty-five equations showing the formation of the salts indi-
cated in **77**, by the above method.

6. Place about 10 c.c. of dilute sulphuric acid in beaker on
wire gauze on lamp-stand.   Add an equal bulk of water, heat
nearly to boiling, and add zinc oxide little by little, with much
stirring, until there is a decided excess present.   Filter into
test-tube, add one drop of dilute sulphuric acid, boil down to
small bulk, cool, and crystallize.   The product is zinc sulphate,
known as **white vitriol**, having the formula $ZnSO_4 + 7 H_2O$.   See
Lab. Ex. No. 6, part 8.

7. Repeat exactly, making use of magnesium oxide with sulphuric acid.

8. Write in Part III, after the description .of the work, twenty-five equations showing the formation of the same salts indicated in **79**, by this method.

Questions on Exercise No. 11. What is the action of a metal on an acid? (**76**). What is an acid? (**63**). What is a base? (**64**). What is a salt? (**66**). What is a basic oxide? (**67**). What gas is generally given off when a metal acts with an acid? (**76**). Under what conditions is no hydrogen given off in this class of action? (**75**). How many grams of HCl would be necessary to combine exactly with 10 g. of iron? (**252**). What is green vitriol? (**796**). What is formed when magnesium dissolves in HCl? What is the action of a basic oxide on an acid? (**78**). What is always formed in this kind of action? How many grams of zinc oxide would be necessary to form 10 g. of zinc sulphate? (**252**). Write equations showing the formation of any salt in two different ways (**76, 78**). What is white vitriol? (**718**). If a rust spot on white cloth is due to a basic oxide of iron, how might it be removed?

LABORATORY EXERCISE No. 12

The Action of Acids on Bases and on Carbonates (80–82)

Materials. Sodium carbonate, Na_2CO_3.

Apparatus. Lamp-stand; wire gauze; evaporating-dish; stirring-rod; test-tubes.

Definitions. Alkali (65). Base (64).

> **Neutral,** reacting neither acid nor alkaline toward litmus or other indicator.
>
> **Neutralization,** the process of rendering a solution inactive toward litmus paper or other indicator.
>
> **Indicator.** Any substance used for the purpose of indicating whether a substance reacts acid or alkaline, *e. g.,* litmus paper or solution. Congo red, phenol-phthalein solution, methyl orange.

1. Place about 5 c.c. of sodium hydroxide solution from reagent bottle in porcelain dish on ring of lamp-stand. Add an equal amount of water. Now add dilute hydrochloric acid little by little until a small piece of litmus paper just turns red. It is evident now that you have too much acid present.

Take a small quantity of the sodium hydroxide solution in a test-tube and dilute it with five times its bulk of water. Add this solution little by little with much stirring until the paper just turns blue. You now have too much alkali. Dilute some more of the hydrochloric acid with ten times its bulk of water and add it very cautiously until a fresh piece of litmus paper turns red. This solution will be neutral enough for our purpose, but if you are very careful it will be possible for you to show a red and a blue paper in the liquid at the same time; the liquid will then be quite neutral.

2. Filter the liquid, replace it in the evaporating-dish, and boil it down to dryness. Heat the dish red-hot for five minutes. The product is common salt, NaCl. Taste it. If you were not particular to have the liquid either exactly neutral or slightly acid, it will not taste like good salt but will have a slight soapy taste.

3. In Part III, after a description of the above work, write twenty-five equations illustrating the formation of the same twenty-five salts indicated in **77**, by the above method.

Preparation of Salts by Treating an Acid with a Salt of a More Volatile Acid (82)

One acid is said to be more **volatile** than another if, when the two are heated together, the first escapes before the second. When an acid is mixed with a salt of another acid, we essentially have two acids present. If the mixture be heated, the more volatile acid will escape, leaving the second acid to combine with the base of the salt. The method is only effective when there is a great difference in the degree of volatility of the two acids concerned (**83**).

Carbonic acid, H_2CO_3, is so unstable that it virtually cannot exist in the free condition, although its salts, the carbonates, are very stable. Therefore, when a carbonate is treated with almost any acid, carbon dioxide is set free and the action goes to completion (**83**).

4. Dissolve ¼ t.t. full of sodium carbonate in test-tube full of water in beaker on wire gauze on lamp-stand with the aid of heat. Decant into two test-tubes.

5. To one portion, in beaker on wire gauze, boiling hot, add dil. HCl little by little until effervescence nearly ceases on addition. Boil down to dryness and heat the dish red-hot.

6. Repeat, using dilute sulphuric acid, but adding it very much more slowly, being very careful not to get too much acid. Boil down carefully to a hot saturated solution. Filter into test-tube and crystallize.

Questions on Exercise No. 12. What is an alkali? (65); a base? (64). What is the action of an acid on a base? (80). What is first formed? What else is formed? When is a liquid said to be neutral? What is meant by "decant"? In 1, just before the solution became neutral, there was a slight effervescence; to what was it due? Why was it desirable to have the solution slightly acid rather than slightly alkaline? When is one liquid said to be more volatile than another? What is the effect of mixing an acid with a salt of a more volatile acid? (82). If the more volatile acid is unstable, what products may be given off? Name some non-volatile acids; some acids that are volatile and stable; some acids that are volatile and unstable (83). What is the effect of adding an acid to a carbonate? How many grams of sodium carbonate would be necessary to form 10 g. of sodium chloride? (252). What is an indicator?

LABORATORY EXERCISE No. 13

Determination of the Strength of Acids and Alkalies. Titration ·

Materials. Standard solution of 1/10 normal hydrochloric acid; standard solution of 1/10 normal sodium hydroxide; vinegar; cider; lime-juice; household ammonia; litmus solution; Congo red.

Apparatus. Two burettes and supports for standard solutions; beaker; stirring-rod; pipettes—1 c.c., 5 c.c., 10 c.c.

Definitions. Standard solution, one containing a known weight of substance per cubic centimeters. Normal acid solution, one containing 1 g. of replaceable hydrogen per liter. A normal solution of hydrochloric acid contains 36.45 g. of acid per liter; this would contain just 1 g. of acid H per liter. Normal sodium hydroxide solution is made by dissolving 40 g. of pure NaOH in 1 liter of water. Since 40 is the molecular weight of NaOH, this would exactly neutralize an equal volume of normal HCl.

Tenth normal solution contains 1/10 as much material dissolved as the normal solution.

Titration. The process of estimating the quantity of a substance present by adding a standard solution from a burette, until the reaction is complete as shown by some kind of indicator.

Pipette. A glass tube, by means of which definite volumes of a liquid may be handled.

1. By means of the pipette transfer exactly 1 c.c. of dil. HCl from the reagent bottle to a beaker. Add about 100 c.c. of distilled water and 3 or 4 drops of an indicator. Fill the burette above the mark and run off the excess of liquid until the lowest point of the visible surface is just level with the first mark. Place the beaker on a piece of white paper directly under the tip of the burette (Fig. 14). By means of the pinch-cock or stop-cock allow the alkali to run slowly into the beaker, with constant stirring until the color just changes.

2. If the solution of alkali was exactly 1/10 normal, 1 liter would contain 4 g. of sodium hydroxide; 1 c.c. would therefore contain .004 g. NaOH. Each cubic centimeter is exactly equal to 1 c.c. of 1/10 normal HCl, which would contain .003645 g. of HCl; multiply this number by the number of cubic centimeters used and obtain the number of grams of HCl in the volume of acid tested. This weight, divided by the weight of the acid tested and multiplied by 100, would give the per cent of HCl in the dilute acid tested.

FIG. 14

3. To get the weight of a cubic centimeter of the acid being examined, weigh exactly 100 c.c. on a platform balance and find the weight of 1 c.c.

4. To determine the strength of an alkaline solution measure a definite quantity of the alkali, transfer to a beaker, dilute with water, add indicator, and titrate with standard acid.
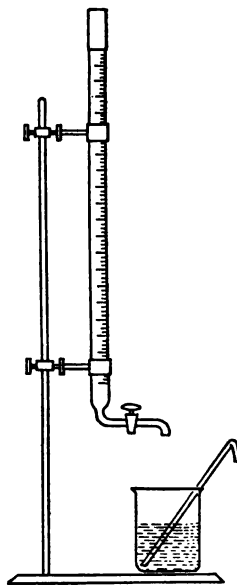
5. Sooner or later during the course in chemistry determine the per cent of the following substances in solution, filling out the table:

Substance Tested	Volume	C.c. Stand. Acid or Alk.	Wt. 1 c.c.	Equiv. Acid or Alk.	Percentage
Dil. HCl					
Dil. HNO₃					
Vinegar					
Cider					
NaOH Solution					
Household Ammonia					

Questions on Exercise No. 13. What is a standard solution? What is a normal acid solution and how is it made? What is a normal alkali solution? How many grams of acid would there be in 1 c.c. of a 1/10 normal solution of sulphuric acid? *Ans.* A normal solution of sulphuric acid must contain only 1 g. of replaceable H. The molecular weight 98 g., dissolved in 1 liter, would give 2 g. replaceable H; therefore, a normal solution must contain ½ molecular weight in grams. 1 c.c. of 1/10 normal acid would therefore contain .0049 g. of the acid. 1 c.c. of dil. HCl weighs 1.09 g. It required 37 c.c. of 1/10 normal NaOH solution to neutralize it. What per cent of HCl did it contain? The acid of vinegar is acetic acid, $HC_2H_3O_2$. It contains but one replaceable H. 10 c.c. of 1/10 normal NaOH would equal how many grams of this acid? How could you determine the relative values of "household ammonia" and the concentrated ammonia of the laboratory?

LABORATORY EXERCISE No. 14

The Formation of Salts by the Mixing of Two Solutions that Combine to Form an Insoluble Compound; Also by Fusing Together Basic with Acidic Oxides (86–90)

Materials. Barium chloride solution; calcium chloride; sodium carbonate; sodium peroxide; silica; litharge; potassium chromate; chromium trioxide; lead nitrate.

Apparatus. Test-tubes; lamp-stand; iron crucible; filter-flask; funnel.

Solubility rule. All the hydrogen, sodium, potassium, and ammonium compounds are soluble; also the chlorates, acetates, and nitrates, and all the chlorides except those of silver, lead, and mercurous mercury (87).

1. Dissolve separately about 5 g. each of sodium carbonate and anhydrous calcium chloride. Heat the clear solutions nearly to boiling and mix them in a 200-c.c. bottle. The precipitate which first forms, if it looks gelatinous, is calcium carbonate in the colloidal condition. Shake or stir it for a moment and it will change to a finely divided precipitate. Filter with the suction filter, using a clean filt r-flask. If the filtrate does not run through perfectly clear, refilter it through an ordinary filter. It should contain a slight excess of sodium carbonate. Add a few drops of HCl, which should cause a slight effervescence, and boil the solution down to dryness in the evaporating-dish. The solid which remains is common salt. The material on the suction filter is calcium carbonate, also known as "**precipitated chalk.**"

2. Make the following mixtures in test-tube and state in each case what the precipitate must be, also what soluble salt must be in solution.

When mixing reagents in a test-tube, place about 5 c.c. of the solution to be tested in the tube, **fill the tube about half full of water.** Mix thoroughly by shaking the tube, or, better, by covering with the thumb and inverting once. Add the second reagent a **drop or two at a time,** mixing after each addition, until you ascertain what the result is going to be. Then add an excess and mix again.

(*a*) Barium chloride with sulphuric acid; (*b*) barium chloride with potassium chromate; (*c*) potassium chromate with lead nitrate; (*d*) lead nitrate with sulphuric acid; (*e*) sodium carbonate with barium chloride.

3. In Part III, after the description of the above work, write twenty-five equations showing the formation of the twenty-five salts indicated in **77**, by this method.

4. Place in the iron crucible about 3 g. of sodium peroxide

and 4 g. of chromium trioxide.   Mix these thoroughly with the
stirring-rod.   Heat if necessary to start the reaction.   After
the reaction is over add $\frac{1}{2}$ t.t. of water and boil for one minute.
Filter through an ordinary filter into test-tube and boil down
until the salt crystallizes out on cooling.   The product is sodium
chromate, $Na_2CrO_4 + 10\ H_2O$.

5. Grind together in the mortar a small quantity of silica
and an equal bulk of lead oxide (litharge).   This mixture, when
heated, forms a lead glass.   A very small quantity may be
heated in a sealed tube with the flame of the blast lamp.

$$PbO + SiO_2 = PbSiO_3.$$
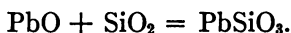
Or the inside of a small scorifier may be covered with the mix-
ture in a moist condition and heated in a muffle-furnace.   The
lead silicate will form a glaze (566).

6. In Part III, after a description of the above work, write
equations showing the formation of the silicates, chromates,
and phosphates of the same five basic radicals indicated in 92,
by this method.

Questions on Exercise No. 14.   State the full solubility rule (87).
What is the effect of mixing two solutions one of which contains the basic
and the other the acid radical of an insoluble compound? (86).   How did
you make barium sulphate?   Mention ten other mixtures that would have
produced the same result.   Describe lead chromate, calcium carbonate,
and barium carbonate.   What is formed when a basic oxide is fused with
an acidic oxide? (91).   In 1, why should the filtrate be acidified with HCl?
If 5 g. of sodium carbonate had been used, how many grams of calcium
chloride should have been added in order that there should not be an
excess of either material? (252).   Name the insoluble sulphates; insoluble
chlorides; soluble hydroxides; insoluble phosphates (87).   What are the
general conditions necessary for the formation of precipitates? (85).
Any oxygen salt may be considered as made up of what two kinds of
compounds? (91).   Write equations showing the formation of any
oxygen salt in six different ways.   What is "precipitated chalk"?   What
is the common name of lead chromate? (817).   For what is it used?

LABORATORY EXERCISE No. 15

Preparation and Properties of Chlorine

Materials.   Manganese dioxide; sodium chloride; potassium
    chlorate; chlorine water; colored cloth; paper with print-
    ing; paper with writing-ink marks; silver nitrate.

Apparatus. .Test-tubes.

Caution. When smelling unknown substances, first fill the lungs with air, then waft some of the unknown odor toward the nose. **Do not smell the pure gas.**

In this exercise, as well as in all others in which disagreeable odors are produced, the hoods should be used as much as possible.

Preparation. Chlorine is commonly prepared in the laboratory by removing the hydrogen from hydrochloric acid. This process is known as oxidation and may be accomplished by almost any oxidizing agent (**115**). It may also be prepared by treating any chloride with an oxidizing agent in the presence of sulphuric acid (**130**).

1. Cover the bottom of a test-tube with powdered MnO_2. Add $\frac{1}{2}$ in. of dil. HCl, shake, and warm gently. Note the color, odor, and effect on moist litmus paper of the escaping gas (**128**).

2. To $\frac{1}{2}$ in. of conc. HCl in test-tube add a few drops of conc. HNO_3. Warm and note what gas is given off (**128**).

3. If conc. H_2SO_4 be mixed with NaCl, what gas should be given off? Place $\frac{1}{4}$ in. of common salt, NaCl, in test-tube, add 2 drops of water and an equal bulk of conc. H_2SO_4. Heat. What is the gas? (**83**).

4. If an oxidizing agent had been present in the above mixture would the same gas have been evolved? Place a small quantity of NaCl in test-tube with an equal bulk of MnO_2. Moisten with 2 or 3 drops of water and add an equal bulk of conc. H_2SO_4. Warm and identify the escaping gas (**130**).

5. Fill a test-tube with chlorine water and place in it bits of colored cloth, and paper with printing and writing-ink marks. Let it stand a week if necessary (**349**).

6. In separate test-tubes add silver nitrate solution to chlorine water, dil. HCl, and sodium chloride solution. Shake the solutions thoroughly and heat a little. What is the precipitate in each case? Decant the liquid from the precipitate in each tube and add ammonium hydroxide. Shake thoroughly. Then acidify each tube with dil. HNO_3. What is the precipitate that reforms in each case? (**347**).

7. Write in Part III, after the description of the above work,

ten equations illustrating the formation of chlorine from HCl by the use of ten different oxidizing agents (128). Also write five equations showing the formation of chlorine from five different chlorides by the use of five different oxidizing agents in the presence of sulphuric acid (130).

Questions on Exercise No. 15. Represent all reactions involved in this exercise by equations. How may hydrogen be removed from hydrochloric acid? (128). Name ten oxidizing agents and show by equations how they oxidize (115). How many grams of MnO_2 would be necessary to form 10 g. of chlorine? (262). If HCl were added to potassium chlorate, what other acid should theoretically be formed? Suppose an excess of sulphuric acid were added to a mixture of sodium nitrate, magnesium chloride, and potassium acetate, and heated, what products would escape and what would finally be left? (83–84). What kinds of colors does chlorine bleach? (349). When nitric acid is added to ammonium hydroxide what salt is formed? What is the precipitate when $AgNO_3$ is added to a chloride in solution? (347). When nitric acid is added to an ammonium hydroxide solution of AgCl what is the precipitate? How might ink marks be removed from paper or cloth? (349).

LABORATORY EXERCISE No. 16

Preparation and Properties of Hydrochloric Acid (351–355)

Materials. Sodium chloride; iron filings; silver nitrate solution.
Apparatus. Lamp-stand; flask; wire gauze; funnel-tube; glass bends; bottles; rubber connectors; rubber stoppers.

1. Set up the apparatus as indicated in the sketch (Fig. 15). *A* contains about 20 g. of sodium chloride; *B* is empty; *C* contains water, but the surface must not quite touch the glass tube; *D* has no rubber stopper and contains 10 c.c. of ammonium hydroxide solution. The funnel-tube must go to the bottom of the flask.

2. Add 8 c.c. of water to the flask through the funnel and be sure that it wets the salt all through. Then add 25 c.c. conc. sulphuric acid.

3. *B* becomes filled with HCl gas at once. The gas is absorbed in the water in *C*. What are the white fumes in *D*?

4. Place a low flame under the flask, remove the bottle *B*, and replace it with another. Fill several bottles in this way

with HCl gas. Keep them right side up and covered with glass plates. In the meantime notice what is going on in the water just below the end of the tube in *C*.

5. Draw out the end of a glass tube 8 or 9 in. long to a very small size, but be sure there is a hole through it. Pass the drawn-out end through one hole of a two-hole stopper and stop up the other hole with a sealed tube; quickly insert the stopper in one of the bottles filled with HCl gas and invert it so the long end of the tube will project downward into a large
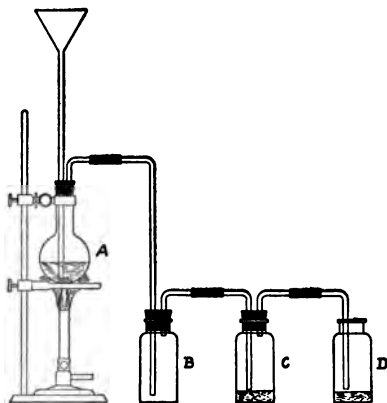
FIG. 15

bottle filled with water. The water will soon rise and produce a fountain in the bottle. If it is slow to start, allow some cold water to run over the acid bottle. (See Fig. 16.)

6. Place about 5 c.c. of strong ammonium hydroxide in a small bottle, shake it about, and pour it out. Invert over it a

FIG. 16

covered bottle filled with HCl gas. Withdraw the glass plate between the two.
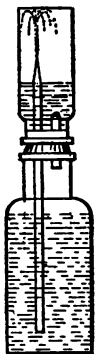
7. Test a bottle of the gas with a burning splint to see if it supports combustion.

8. Test the liquid in *C* with litmus paper. Note the odor of it. Does it smell like the concentrated hydrochloric acid in reagent bottle? Pour some of it on iron filings in test-tube and prove that the gas given off is hydrogen. Test a portion of it with silver nitrate and note that the precipitate dissolves in ammonium hydroxide. Heat some with a little manganese dioxide and note that chlorine is given off.

9. The white solid which separates in the flask is acid sodium sulphate, $HNaSO_4$. (See Acid salt, **642**).

10. In Part III, after the description of the above work,

write equations showing the formation of HCl from ten different chlorides (82).

Questions on Exercise No. 16.   How are acids, other than sulphuric acid, commonly prepared? (82).   In what other ways might acids be prepared? (132).   Why must the funnel-tube go to the bottom of the flask?   Why is water put into the flask?   Why is hydrogen chloride visible in moist air? (352).   What are the white fumes in D? (353).   Represent all reactions involved in this exercise by equations.   How many grams of hydrogen chloride could be made from 20 g. of salt? (252).   How many liters would this gas occupy at normal temperature and pressure? (253).   State all the evidence you have that the liquid in D is the same as the hydrochloric acid in the reagent bottle.   How soluble is hydrogen chloride gas in water? (352).   In 5, what makes the water rise into the upper bottle?   How might acids other than hydrochloric be made? (82).   Write equations showing the formation of hydrochloric acid from ten different chlorides.   What would be formed if chlorine were allowed to act on wet phosphorus? (366, 1).

LABORATORY EXERCISE NO. 17

The Preparation and Properties of Bromine and Iodine (356–367)

Materials. Potassium bromide; potassium iodide; starch; manganese dioxide; carbon disulphide; bromine water; chlorine water; alcohol; colored cloth; iodine.

Apparatus. Test-tubes; bulb test-tube; cork stopper with hole, to fit bulb test-tube; medium glass bend.

Definitions. Sublimation. The process of distilling a solid in such a way that the vapor condenses directly to the solid form.

Sublime. To distil a solid in such a way that the vapor condenses directly to the solid form.

Sublimate. The solid product formed by sublimation.

1. Place in a bulb test-tube 2 g. of potassium bromide, 2 of manganese dioxide, and 10 drops of water (130).

2. Fit the tube with **cork** stopper and medium glass bend, as in Fig. 10.   Fill a large bottle with water and stand in it a test-tube containing a few cubic centimeters of water.   Place the end of the glass bend well down in the test-tube and see that it does not quite touch the water (Fig. 17).

3. Remove the cork stopper and add about 5 c.c. of conc.

sulphuric acid to the mixture of manganese dioxide and potassium bromide. Replace the stopper firmly. The whole will remain supported by itself.

4. Holding the burner in the hand, warm the tube throughout its whole length until 5 or 6 drops of bromine have distilled over. **Do not inhale the vapor of bromine. Do not get liquid bromine on the hands.**

5. Remove the tube from the bottle and examine the drop of bromine. Fill the tube half full of water and shake thoroughly to dissolve the bromine and form bromine water. Use t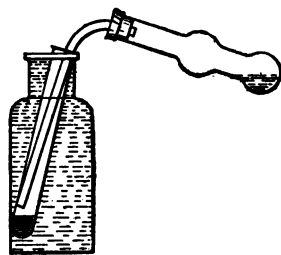his bromine water in the following experiments. If you need more bromine, use the bromine water from the reagent bottle.

Fɪɢ. 17

Caution. Carbon disulphide is extremely inflammable. Do not have a flame near when using it in the next experiment.

6. Test the bleaching power of bromine water just as you did with chlorine water. Add some carbon disulphide, about 4 c.c., to a tube ¼ full of water, and shake it thoroughly. Note that the carbon disulphide does not dissolve in the water, but ultimately settles out in a clear globule at the bottom of the tube. Now add some bromine water and shake again. Bromine is soluble in carbon disulphide, and, since the latter is insoluble in water, the color of the bromine is soon transferred to it, changing it to a yellow or a red, according to the quantity of bromine present. This is a common test for free bromine.

7. Dissolve 1 g. of potassium bromide in about 5 c.c. of water in a test-tube, add carbon disulphide, and shake. There is no color change, therefore no free bromine. Now add some chlorine water and shake again.

8. Fit a bulb test-tube with a **cork** stopper and straight glass delivery-tube 3 in. long. Place in the tube 1 g. of potassium iodide, 2 of manganese dioxide, and 10 drops of water. Add about 5 c.c. of conc. sulphuric acid. Replace the stopper firmly and invert a dry test-tube over the delivery-tube. (See Fig. 18) (**130**).

9. Holding the generating-tube in the wire test-tube holder, heat it carefully at first, and finally boil the liquid to drive the iodine up into the inverted tube. The action is over when the purple color disappears from the generating-tube.

10. Fill the receiving-tube half full of water, cover with the thumb, and shake thoroughly. What does this show you about the solubility of iodine in water? The brown solution is iodine water and may be used in some of the following experiments.
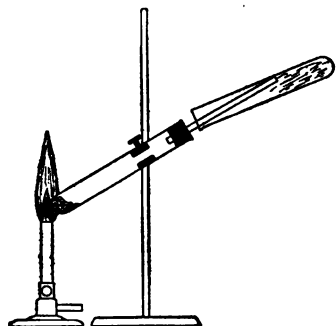
11. Place a small crystal of iodine (from reagent bottle) in a dry test-tube and heat it gently. Does it melt, boil, vaporize, or sublime? Let the tube cool and examine the inside carefully. Fill it half full of water and heat it to boiling. Is iodine volatile with steam? Add 3 c.c. carbon disulphide and some iodine water to a tube half full of water and shake thoroughly. This is a common test for free iodine.

Fig. 18

12. Dissolve 1 g. of potassium iodide in 5 c.c. of water in test-tube. Add carbon disulphide and a little chlorine water and shake thoroughly. What did the chlorine do to the potassium iodide? Repeat, using bromine water.

13. Heat a test-tube full of water in beaker to boiling. Mix 1 g. of starch with 5 c.c. of water in test-tube and pour the mixture into the boiling water. This forms a starch paste solution. To a very small quantity of this solution in a test-tube half full of water add a drop of iodine water. This is the best test for free iodine (370).

14. Test the solubility of iodine in alcohol, also in water containing a little potassium iodide. A solution of iodine in alcohol is known as tincture of iodine.

15. Obtain some finely divided iodine by adding nitric acid to about 1 g. of KI dissolved in 10 c.c. of water. Fill the tube with water, let settle, and decant. Repeat the washing and decantation. Fill the tube half full of water and pass in

H_2S through a glass tube going to the bottom of the iodine tube until all of the brown color due to the I is removed. What is the precipitate? How does it oxidize? (**115**). What acid is formed? (**376**).

16. Write equations showing the formation of bromine and iodine from five different bromides and five different iodides by the use of MnO_2 and H_2SO_4 (**130**).

Questions on Exercise No. 17. What are the **halogens**? (See Chap. XXVI.) How might bromine be obtained from hydrobromic acid? (**129**). What oxidizing agents would remove the hydrogen from hydrobromic acid? (**115**). Is hydrobromic acid more or less stable than hydrochloric acid? (**363**). What takes place when chlorine water is added to a solution of a bromide? Is hydriodic acid more or less stable than hydrobromic acid? (**374**). Could this acid be made by the action of sulphuric acid on an iodide? Is iodine volatile with steam? How may iodine be separated from an iodide? (**130**). What is the effect of adding either chlorine or bromine water to a solution of an iodide? Describe tests for both free and combined iodine (**370**). What is the effect of passing hydrogen sulphide into iodine suspended in water? What would be formed if phosphorus were added to iodine water? (**376**). Name three good solvents for iodine. Represent all the reactions involved in this exercise by equations. How many grams of phosphorus would be necessary to form 10 g. of hydriodic acid? (**252, 376**). How could you test a substance for the presence of starch? (**370**).

Laboratory Exercise No. 18

Experiments with Sulphur (386–393)

Materials. Sulphur; carbon disulphide; iron filings.
Apparatus. Test-tubes; evaporating-dish; combustion spoon; mortar; water-pan.
NOTE. **Sulphur is insoluble in water.** Do not try to wash with water, tubes that have contained melted sulphur.

1. Grind together in the mortar about 1 g. of sulphur and 5 c.c. of carbon disulphide. Filter a few drops of this solution through a dry folded filter-paper, held in the hand, upon a dry glass plate. After the liquid has evaporated examine the larger crystals with the unaided eye and the smaller ones under the microscope. What is the general shape? Make a drawing of them (**387, 1**).

2. Spread a large piece of paper on the table. Stand the burner on it in an inclined position. Fill a dry test-tube ⅔ full of clean lumps of sulphur. Holding it in the test-tube holder, heat it **very slowly and carefully** until the sulphur has all melted to a pale straw-colored liquid. If it becomes dark-colored you have melted it too fast. Pour some of this light-colored liquid into water in the water-pan. Now heat the rest very much hotter and note the changes it undergoes. When it begins to boil pour it in a thin stream into the water in the water-pan. It will probably take fire, but that does not matter. Remove the product from the water and examine it at once. Keep this product for several days and note the changes (387, 3).

3. Let a tube half full of melted sulphur stand until crystals are seen lining the inside of the tube. Then pour the remaining liquid sulphur into the water in the water-pan and examine the crystals left in the tube. These are of the mono-clinic variety (387, 2). **Never pour sulphur into the sink.**

4. Place a small quantity of sulphur in the bowl of the combustion spoon—not enough to fill it when melted—and heat the spoon until the sulphur is burning violently. Lower the burning sulphur into a bottle. Keep the bottle covered with a glass plate. Let the sulphur burn as long as it will. What product is formed here? (388). Is it a solid, a liquid, or a gas? Is it acidic or basic? Will it dissolve in water? What effect has it on litmus paper?

5. Weigh out approximately 6 g. of iron filings and 3 g. of sulphur. Grind these together thoroughly in the mortar. Transfer the mixture to the tube in which you melted the sulphur and from which as much sulphur has been removed as possible by pouring it out in the melted condition. Heat the bottom of the tube as hot as possible in the hood until the reaction begins, and then remove it from the flame and observe the progress of the reaction. The compound that is formed is ferrous sulphide. When the tube is cool break it and remove the solid lump. Save it for the next experiment.

6. Write ten equations showing the formation of sulphides by the direct union of sulphur with metals.

Questions on Exercise No. 18. What liquid readily dissolves sulphur? Represent all the reactions involved in this exercise by equations. Draw a diagram of the crystals obtained by the evaporation of the carbon disulphide solution. Describe all the changes that sulphur undergoes when very slowly heated (387). Describe three different varieties of sulphur. How would you change any one of them into any other? What is formed when sulphur burns in air? (388). What is formed when this oxide is dissolved in water? What is the effect of adding an oxidizing agent to this solution? (402). How many grams of ferrous sulphide could be made from 10 g. of iron? (152). How many liters of hydrogen sulphide could be obtained from this amount of ferrous sulphide? (153). How could you readily extract the sulphur from black gunpowder?

LABORATORY EXERCISE No. 19

Preparation and Properties of Hydrogen Sulphide (394–399) and Sulphur Dioxide (400–405)

Materials. Ferrous sulphide, from last experiment; cupric sulphate solution; barium chloride solution; lead nitrate solution; potassium permanganate solution; potassium dichromate solution; cadmium sulphate solution; cylinder of liquid sulphur dioxide.

Apparatus. Bottles; beaker; evaporating-dish; test-tubes; No. 3 one-hole rubber stopper; delivery-tube.

Caution. As far as possible all experiments with H_2S and SO_2 should be performed in the hoods.

1. Fit a test-tube with a rubber stopper and delivery-tube. Break up the lump of ferrous sulphide obtained in the last exercise and place it in the tube. Cover it with water and add equal bulk of dil. H_2SO_4 (398). Note the odor of the escaping gas. Fill a test-tube, by upward displacement of air, with the gas and ignite it. What are the products? What is the white deposit left on the inside of the tube? (396).

2. Pass some hydrogen sulphide from the source of supply in the hood into a test-tube half full of water containing a few drops of cupric sulphate solution. Let the gas run for several minutes. The tube delivering the H_2S should be of glass and reach to the bottom of the test-tube. Filter off the black precipitate and note that the blue color due to the cupric sulphate

solution has entirely disappeared.   The copper may be entirely removed from the solution in this way (396).

3. In a similar way pass H_2S into solutions of lead nitrate and cadmium sulphate.   Are all sulphides black?

4. Test the action of a water solution on litmus paper. What would be formed if this gas were passed into a solution of sodium hydroxide; into ammonium hydroxide? (396).

5. Fill several bottles with sulphur dioxide from the cylinder in the hood.   Keep them upright and covered with glass plates.   Be sure to turn off the gas at the cylinder.   Invert one of the bottles in a dish of water.   The water rises in the bottle.   What does this indicate? (402).   Fill another bottle one quarter with water, cover tightly with the palm of the hand, and shake it thoroughly.   What does the suction on the hand indicate?   Test the resulting liquid with litmus paper.   What acid is in the water?   Represent its formation by an equation. Save the solution (402).

6. Add a few drops of conc. HNO_3 to a bottle containing SO_2.   What are the red fumes?   What kind of action took place?   Add water and some $BaCl_2$ solution.   A white precipitate indicates the formation of H_2SO_4.   What did the nitric acid do to the sulphur dioxide? (402).   Pour a little potassium dichromate into a solution of SO_2 in water.   Repeat, using a few drops of potassium permanganate solution.   Both of these substances are oxidizing agents.   They oxidize the sulphurous acid to sulphuric.   Prove this by adding a little barium chloride and noting the white precipitate.   Indicate these reactions by equations (403).

7. Sulphur dioxide may be prepared by reducing hot concentrated sulphuric acid with metals.   Place a bunch of copper wire in the bottom of a test-tube, cover it with concentrated sulphuric acid, and heat to boiling.   Prove that the gas given off is SO_2 (404, 4).

8. Neutralize a small quantity of strong sulphur dioxide water with NaOH and evaporate to dryness in the evaporating-dish.   The product is sodium sulphite, Na_2SO_3.   If this be treated with almost any acid, SO_2 is set free (404, 2).

9. In Part III, after the description of the above work,

represent by equations the formation of hydrogen sulphide from five different sulphides (398); the reduction of concentrated sulphuric acid with the formation of sulphur dioxide, making use of five different metals (404, 4); the oxidation of sulphur dioxide to sulphuric acids or sulphates by the use of five different oxidizing agents (402).

Questions on Exercise No. 19. How may acids other than sulphuric be prepared? (82). How did you prepare hydrogen sulphide? (398). Represent by equations all the reactions involved in this exercise. How would you obtain hydrogen sulphide from sulphur? How many grams of iron would be necessary to produce 10 liters of hydrogen sulphide at normal temperature and pressure? (253). What is formed when hydrogen sulphide burns? (396). What evidence have you that hydrogen sulphide water has acid properties? State three ways in which sulphur dioxide may be made (404). How could you make sodium sulphite? Show the formation of sulphur dioxide by the oxidation of metals by means of sulphuric acid. How many grams of copper would be necessary to form 10 liters of sulphur dioxide? (253). Describe the preparation of sulphuric acid. How can you prove that nitric acid changes sulphurous acid to sulphuric acid? (403).

LABORATORY EXERCISE No. 20

Preparation and Properties of Sulphuric Acid (407–413)

Materials. Sulphur; barium chloride solution; bromine water; cupric sulphate solution; zinc sulphate; iron wire; potassium permanganate solution; cylinder of liquid SO_2.

Apparatus. Combustion spoon; test-tubes; bottles.

Caution. **Do not spill sulphuric acid.**

Do not pour water into sulphuric acid.

Do not pour boiling sulphuric acid into water.

1. Place about ½ in. of water in a large bottle. Place a small quantity of sulphur in the combustion spoon, less than will fill it when melted, and heat it until it is all melted and blazing. Suspend the blazing sulphur directly over the water, keeping the bottle covered, until it will burn no longer. Remove the spoon, cover the bottle with the hand, and shake thoroughly to dissolve the sulphur dioxide in the water. This forms a solution of sulphurous acid. To a portion of this so-
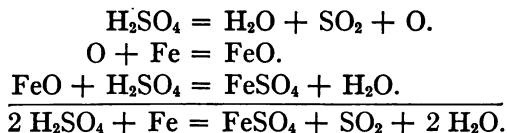
lution add a few drops of barium chloride solution. What does the slight white precipitate indicate? (388).   Then add a few drops of concentrated nitric acid.   What does the additional white precipitate indicate? (402).

2. Add barium chloride and bromine water to a strong solution of sulphur dioxide in water (402).   Repeat, using potassium permanganate solution (402).

3. Notice the weight of the concentrated sulphuric acid in the reagent bottle, also its oily nature.   Pour some concentrated sulphuric acid into 10 c.c. of water in a test-tube.   Put pieces of wood and paper in hot concentrated sulphuric acid.   Dilute some sulphuric acid with ten volumes of water and write on paper with it.   Heat the paper (409).

4. Ascertain the effect of cold and hot concentrated sulphuric acid on iron wire.

Hot concentrated sulphuric acid is an oxidizing agent according to the equation:

$$H_2SO_4 = H_2O + SO_2 + O.$$
$$O + Fe = FeO.$$
$$\underline{FeO + H_2SO_4 = FeSO_4 + H_2O.}$$
$$2\,H_2SO_4 + Fe = FeSO_4 + SO_2 + 2\,H_2O.$$

What is the effect of hot dilute sulphuric acid on iron wire?

5. Systematically dilute some of the acid in 10 t.t.   Find approximately how dilute a solution will give a test with barium chloride (411).

6. Test solutions of cupric sulphate and zinc sulphate with barium chloride.

7. **Test for sulphuric acid or a soluble sulphate.**   Add barium chloride and some hydrochloric acid to the solution to be tested; a white precipitate insoluble in HCl is evidence of the presence of the sulphate radical.

Neutral and alkaline solutions of phosphates or carbonates give white precipitates with $BaCl_2$, but they are soluble in HCl.

8. In Part III, after a description of the above work, write equations indicating the oxidation of hydrogen sulphide, ammonium sulphide, sulphur, and sulphur dioxide to sulphuric acid or a sulphate, by means of nitric acid (133).

Questions on Exercise No. 20. Represent by equations all the reactions in this exercise. What two oxides does sulphur form? (388). Which of these is formed in greatest quantity when sulphur is burned? What evidence have you that there is some of the other formed? When these oxides are dissolved in water, what acids result? (388). How many grams of bromine would be necessary to oxidize 10 g. of sulphur as sulphur dioxide to sulphuric acid? (252). State the test for the sulphate radical (411). What visible effect has concentrated sulphuric acid on organic matter? What is noticed when sulphuric acid and water are mixed? What effect has boiling concentrated sulphuric acid on the metals? (404, 4). What is an oxidizing agent? (108). Name ten oxidizing agents and state how they oxidize (115). Write an equation showing the action of hot concentrated sulphuric acid on copper (404, 4).

LABORATORY EXERCISE No. 21

Composition of the Atmosphere (434-447)

Materials. Anhydrous calcium chloride; barium hydroxide; yellow phosphorus in beads.

Apparatus. Water-pan; filled calcium chloride tube; two 500-c.c. bottles; two No. 8 two-hole rubber stoppers; glass bends; rubber tubing.

1. **Moisture.** Weigh accurately a filled calcium chloride tube and connect it, as shown in Fig. 19, with two 500-c.c. bottles.
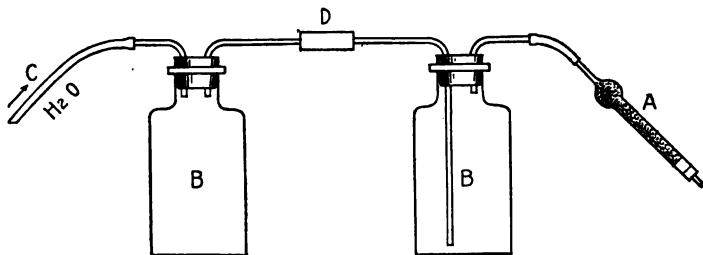

FIG. 19

Connect the tube C with the water faucet and turn on a slow stream of water. The water forces the air in the bottles slowly through the calcium chloride tube. Any moisture will be absorbed in the drying-tube. When the first bottle is filled with water disconnect the drying-tube and weigh again. The increase in weight is the amount of water vapor in 500 c.c. of air (671).

2. **Carbon dioxide.** Pure air contains from 3 to 4 parts of carbon dioxide to every 10,000 parts by volume. This is too small a proportion to be readily determined quantitatively by the student. Moisten the surface of one glass plate with NaOH solution and another with $Ba(OH)_2$ solution. Let both plates stand until the next exercise, but notice them from time to time. A white deposit of the carbonate will be seen (**515**).

3. **Oxygen.** Seal the end of a glass tube about 12 in. long and having an inside diameter of about ¼ in. Cut off enough from the open end to leave a sealed tube 10 in. long. Dry a pellet

FIG. 20

of yellow phosphorus about the size of a grain of wheat, by touching it to filter-paper, and by means of the forceps drop it into the tube. Insert a piece of copper wire 2 or 3 in. long, bent sufficiently so that it will not slip out. By means of the handle of the combustion spoon push the wire in to the end of the tube, as in Fig. 20; it will be sufficient to hold the phosphorus in position. Place the finger tightly over the open end of the tube. Holding the open end under water in the water-pan, with the tube in an inclined position, melt the phosphorus by the careful application of the Bunsen flame and cause it to run down over half the length of the tube. After a minute or two slowly immerse the whole tube in the water and remove the finger. Allow the tube to lie in the water for five minutes. Then remove it and measure the length of the tube which is filled with water. It should measure about 2 in., showing the air to contain about one-fifth oxygen.

Questions on Exercise No. 21. What change takes place in calcium chloride when left exposed to the air? What is meant by "deliquescence"? (**176**). How may the moisture be removed from air or other gases? How is it possible to determine the exact amount of moisture in the air? How does the amount of moisture vary with the temperature? What evidence have you that the air contains carbon dioxide? What is the white incrustation which is commonly seen about the mouth of the sodium hydroxide bottle? How may the oxygen be removed from a portion of the air? What oxides does phosphorus form when burned?

(470). What acids are formed when the oxides of phosphorus are dissolved in water? (470). What is the proportion of oxygen in the air? (434). What is the gas which is left in the bottle? Is it pure nitrogen? (421).

LABORATORY EXERCISE NO. 22

Preparation and Properties of Nitrogen and Ammonia (414-433)

Materials. Sodium nitrite; ammonium chloride; calcium hydroxide (dry); ammonium nitrate; ammonium sulphate; litmus solution.

Apparatus. Water-pan; bulb test-tube; rubber stopper; delivery-tube; lamp-stand; bottles; mortar.

1. In the previous experiment the gas left in the tube is known as atmospheric nitrogen. Chemically pure nitrogen may be prepared by heating a solution of ammonium nitrite. As this material is not usually available, a mixture of ammonium chloride and sodium nitrite is used (421, 3). Fit a bulb test-tube with a rubber stopper and delivery-tube, as in Fig. 21. Place in the tube about 1 g. of sodium nitrite and an equal amount of ammonium chloride with 5 c.c. of water.
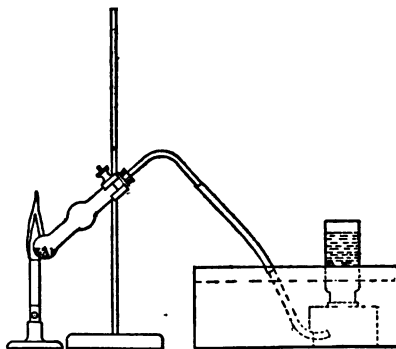

Fig. 21

Heat the mixture carefully and collect the gas over water. This gas will neither burn nor support combustion (421, 3).

2. Place a small quantity of ammonium chloride in the mortar, moisten it with NaOH, and grind for a moment (429). Note the odor of ammonia and the effect of the gas on moist red litmus paper. Hold over the mortar a piece of filter-paper moistened with conc. HCl (426). The white fumes are ammonium chloride formed by the direct union of the ammonia gas with the HCl.

3. Repeat exactly, making use of ammonium sulphate and ammonium nitrate.

4. When an ammonium compound is heated it breaks up into ammonia and the corresponding acid. This is a case of a reversible reaction, for in the colder part of the apparatus the two recombine. Heat a gram or two of ammonium chloride in a test-tube and place in the mouth of the tube a piece of moist red litmus paper. Explain the color change of the paper (429).

5. Mix thoroughly in the mortar about 5 g. of ammonium chloride and 10 g. of dry calcium hydroxide. Transfer the
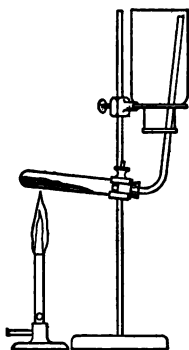

Fig. 22

mixture to a test-tube and add only enough to half fill it. Fit the tube with a rubber stopper and medium bend. Tap the tube in a horizontal position to obtain an air space over the whole of the mixture. Fix it in the clamp of the lamp-stand in a nearly horizontal position with the stopper end lower, as shown in Fig. 22, so that any water formed will not run back on the hot glass. Heat very carefully, holding the burner in the hand, **but not hot enough to cause the flame to turn yellow as a result of melting the tube.** Collect the ammonia by downward displacement of air as shown. A piece of paper, moistened with conc. HCl, held near the mouth of the bottle will smoke when the bottle is filled with the gas.

6. Make an ammonia fountain exactly as you made the HCl fountain (Exercise No. 16, 5). Color the water in the bottle with litmus solution and render it red with a drop of dil. HCl.

7. Invert a bottle of ammonia in a dish of water. Drop some conc. HCl into a bottle of the gas. Test the gas with moist red litmus.

8. Neutralize some ammonium hydroxide from the reagent bottle with nitric acid. Boil down the solution in the evaporating-dish until some of it will solidify on the end of the glass rod. What have you made? Save the product.

9. In Part III, after the description of the work, write ten equations showing the formation of ammonia from ten different

ammonium compounds (429). Also ten equations showing the combination of ammonia gas with ten different acids (426).

Questions on Exercise No. 22. Describe a method of preparing chemical nitrogen as distinguished from atmospheric nitrogen. What is formed when an alkali or an alkaline oxide is heated with an ammonium compound? (429). · What takes place when an ammonium compound is heated? What is meant by a reversible reaction? (72). Explain why, in 4, the red litmus paper first turned blue and then red. Describe tests for both free and combined ammonia (427). How many grams of ammonium chloride would be necessary to form 10 liters of ammonia under normal conditions? (253). What takes place when ammonia gas comes in contact with an acid? (426).

LABORATORY EXERCISE No. 23

Some Oxides of Nitrogen, and Nitric Acid (448–460)

Materials. Ammonium nitrate; scrap copper; sodium nitrite; phosphorus; sodium nitrate; sulphur.

Apparatus. Lamp-stand; water-pan; bottles; rubber stopper and delivery-tube; funnel-tube.

1. Place in test-tube about 1½ in. of ammonium nitrate. Fit tube with stopper and delivery-tube. Fix tube in clamp on lamp-stand in an inclined position, so the bottom of tube comes near the base of the Bunsen flame (see Fig. 21). Heat very carefully until the material is all melted, then only enough to produce a steady evolution of the gas. Excessive heating may produce an explosion. Under no circumstances should the material be heated until it is nearly all gone. The gas given off is nitrous oxide, N_2O. Remove delivery-tube from water-pan before removing the flame (449).

2. Test the solubility of this gas in water. Make the same experiments with it that you did with oxygen. How could you distinguish this gas from oxygen? (449).

3. Fit a small bottle with a two-hole rubber stopper. Through one of the holes pass a funnel-tube. The end of the tube must reach very near to the bottom of the bottle. Through the other pass a short bend, to which a delivery-tube is attached. Place several pieces of scrap copper in the bottle and stand the whole on the lamp-stand with the funnel-tube

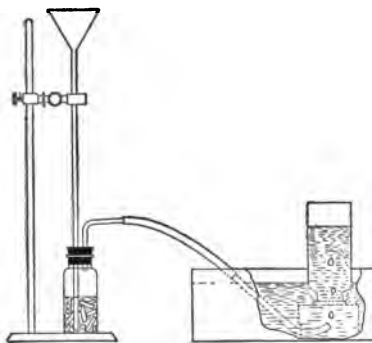passing through a ring to prevent the apparatus from being upset (see Fig. 23). Arrange to collect the gas over water in the water-pan. Add about 20 c.c. of dil. nitric acid and then conc. nitric acid little by little as necessary to produce the reaction. Have all receiving bottles upside down in the pan, and absolutely full of water. Do not allow any air to enter when removing the bottles of gas from the pan (**450**).

FIG. 23

What is the color of this gas? It is called nitric oxide, NO.

Open a bottle of it in the air (**452**). Why was the gas colored brown in the generating bottle at first? Will it support combustion? Test it with very hotly burning phosphorus in the hood. What would be the effect of mixing nitric oxide with oxygen; nitric oxide with nitrous oxide? (**449**).

4. Treat small quantities of sodium nitrite with the different dilute acids in test-tubes. Nitrous acid, HNO_2, is unstable and breaks up into water and nitrogen trioxide (**453**):

$$2\,HNO_2 = H_2O + N_2O_3.$$

5. Fill a large bottle with water. Place in it a test-tube. Fit a bulb test-tube with a **cork** stopper through which passes the short arm of a medium glass bend. Place in this tube 3 g. of sodium nitrate, 5 drops of water, and about 5 c.c. of conc. sulphuric acid. Replace the stopper firmly. (See Fig. 24.)

Place the long end of medium glass bend in receiving-tube. The whole apparatus will support itself. Holding the burner in the hand, heat the mixture carefully until about 1 c.c. of

FIG. 24

nitric acid has distilled over. Satisfy yourself that this liquid is nitric acid by its characteristic action on copper wire (**461**).
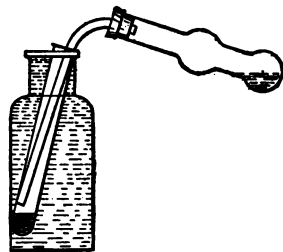
6. After a description of the above work in Part III, write ten equations showing the formation of NO by the action of nitric acid upon ten different metals (459). Also the formation of nitric acid by the action of sulphuric acid upon ten different nitrates (461).

Questions on Exercise No. 23. Represent by equations all the reactions in this exercise. How many liters of nitrous oxide could be prepared from 10 g. of ammonium nitrate? (253). Write equations showing the combustion of carbon, sulphur, and phosphorus in nitrous oxide (449). How could you distinguish between nitrous oxide and oxygen? (449). How many grams of copper would be necessary to prepare 10 liters of nitric oxide? (253). What is the action of an acid upon a nitrite? (456). How is nitric acid prepared? What is a good test for nitric acid? (460).

LABORATORY EXERCISE No. 24

Examination of an Unknown Substance

The object of this exercise is to impress on the student again the necessity for close original observation in all his chemical work; to call his attention again to the fact that every simple experiment that he has done or is going to do is simply a practical way of answering some question concerning the material he is operating on, and it is for him to see what the question is in every case; and that his notes are simply a series of definite *facts* which he has learned by his own observation of the experiments done in answer to the various questions he has had in mind.

Materials. Several unmarked chemical compounds; silver nitrate solution; barium chloride solution; potassium chromate solution.

Apparatus. Sealed tubes; test-tubes.

Definitions. Sublime. A substance is said to sublime when it changes from the solid to the gaseous form and back to the solid on being distilled. Water of crystallization (174). Precipitate (85).

Never attempt to write equations unless there is some definite reaction, the nature of which is known.

1. **Will it melt, boil, vaporize, or sublime?**   Place a small quantity in a sealed tube and heat it as hot as possible, noting results.   Don't mistake a transparent melted solid for water. If any water is present it will distil up on the sides of the tube or perhaps come out in the form of steam.

Leave at least one blank line after every recorded observation where there was a definite reaction, to be filled in later, when the nature of the substance is known, with the equation representing that reaction.

2. **Is it soluble in water, and, if so, to what extent?**   Use very small quantities in testing solubility.   Make the test in both cold and boiling water.   Is it soluble in dilute nitric acid?   How does the water solution affect litmus paper?

3. **How does it affect the flame?**   Heat some on an iron-wire loop which has been thoroughly cleaned by dipping it in hydrochloric acid in test-tube, and washing it.   **Don't clean iron wire by dipping it in the reagent bottle.**

4. **Action of concentrated sulphuric acid.**   This test is for the purpose of ascertaining whether the substance is a salt of a volatile and stable acid, such as nitric, hydrochloric, or acetic. Place about 2 g. of the substance in a test-tube, add one drop of water, and 2 c.c. of conc. H_2SO_4.   Heat carefully and watch for the evolution of a gas or liquid.

5. **Tests with other acids.**   If there was a decided action with sulphuric acid, test portions with dil. HCl.   Carbonates, nitrites, and sulphites will effervesce.

6. **Test for combined ammonia.**   Grind a small quantity of the material in the mortar with NaOH solution.   Smell for ammonia.

7. If the material was soluble in water, test portions of the water solution with the following reagents: silver nitrate, barium chloride with HCl, potassium chromate, hydrogen sulphide gas, dilute sulphuric acid, and ammonium hydroxide.   If it is insoluble in water but soluble in dil. HNO_3, dilute the nitric acid solution and make the above tests.

8. When the examination of an unknown substance is finished, write a clear report of the results and hand it in.

Work very slowly.   Be sure of your facts before recording them.   Repeat tests several times if necessary.

Questions on Exercise No. 24. What class of compounds give water when heated? (**174**). What happens when an ammonium compound is heated? (**429**). What happens to many nitrates when heated? What is the effect of heating a chloride with conc. H_2SO_4; a nitrate; an acetate? (**82**). What is the action of HCl on a carbonate; a nitrite; a sulphite? (**82**). What is the action of sodium hydroxide oñ an ammonium compound? (**429**).

LABORATORY EXERCISE No. 25

Phosphorus and Arsenic (466–476)

Materials. Yellow phosphorus in beads; carbon disulphide; red phosphorus; hydrogen disodium phosphate solution; silver nitrate solution; arsenic trioxide; charcoal; metallic arsenic.

Apparatus. Iron plate; lamp-stand; large dry bottle; test-tubes.

1. Dry about ½ g. phosphorus beads by touching them to filter-paper. Place the dry phosphorus on dry iron plate on lamp-stand, ignite it, and cover with large dry bottle. Let it stand until it ceases to burn and the white smoke has settled. Scrape out the phosphorus pentoxide with a wire, place it on a dry glass plate, and allow 1 drop of water to fall on it. Breathe on some of the product. Do you consider that it has a great attraction for water? Test it with moist litmus paper. What oxides does phosphorus form? (**469**). What acids do these oxides form when dissolved in water? (**470**).

2. Examine the residue left on the iron plate. Note that, while the centre contains some phosphorus pentoxide, it is surrounded by a red substance (**466**). This red material is red or **amorphous phosphorus**. Place the burner directly under the plate and heat it as hot as possible. Note that the red phosphorus is converted to the yellow variety and takes fire.

3. Dissolve one piece of yellow phosphorus in about 4 c.c. of carbon disulphide in test-tube. Pour the solution on a disk of filter-paper supported on ring of lamp-stand in hood, and await developments. **Don't spill any of the solution on your hands or clothes.**

4. To 5 c.c. of hydrogen disodium phosphate solution in test-tube add a few drops of silver nitrate solution. The yellow

precipitate is silver orthophosphate. Add to this a small quantity of dilute nitric acid and shake well. Note the ready solubility of this precipitate in the acid. Add to this carefully, so as not to mix with it, some ammonium hydroxide solution. The precipitate will reappear in the neutral zone between the nitric acid solution in the bottom and the ammonia at the top. Rinse out the bottle containing the phosphorus pentoxide with a little water, place the solution in a test-tube, and add silver nitrate and ammonia as above to prove the presence of the phosphate radical.

5. **Arsenic.** Warm a small piece of metallic arsenic in a sealed tube or test-tube. Let the tube cool. Shake out the arsenic and transfer it to another sealed tube. Heat as hot as possible until no further change takes place. Note the two modifications of arsenic (478).

6. Heat a very minute piece of metallic arsenic in a large dry test-tube. It should take fire and burn, forming a white smoke (479). This smoke condenses to minute crystals on the side of the tube. Examine these crystals through the side of the tube under the microscope. They are crystals of arsenic trioxide (484).

7. Heat a very small quantity of arsenic trioxide in a sealed tube. Note that it sublimes readily. Place a small quantity of the oxide in a sealed tube and above it $1\frac{1}{2}$ in. of broken charcoal. Heat the charcoal red-hot first, and then gradually heat the oxide, keeping the charcoal hot. The vapor of the oxide is reduced as it passes over the carbon (481).

8. Test the solubility of the trioxide in both dil. HCl and NaOH solutions (479). Pass H_2S into the dil. HCl solution (479). What compound would be formed if the oxide were boiled with concentrated nitric acid? (136).

9. Write in Part III equations showing the oxidation of phosphorus and arsenic to the corresponding acids by means of five different oxidizing agents (137).

Questions on Exercise No. 25. Name the elements of the fifth group. What valences have they? What two classes of oxides do they form? (100). What two oxides does phosphorus form? Represent by equations all the reactions involved in this exercise. What acid does phos-

phorus trioxide form with water? (100). What acids does phosphorus pentoxide form with water? (470). How could you convert some yellow phosphorus to the red variety? How could you convert red phosphorus to yellow? What is spontaneous combustion? (316). What does silver orthophosphate look like? Describe a test for the phosphate radical (472). What are the two modifications of arsenic? (478). What oxides does arsenic form? What acids would these oxides form with water? (479). What salt is formed when As_2O_3 is dissolved in HCl? (479). What salt is formed when the same oxide is dissolved in NaOH? What compound is formed when metallic arsenic is burned in air? What is formed when arsenic is dissolved in nitric acid?

LABORATORY EXERCISE No. 26

Carbon (498–512)

Materials. Powdered charcoal; animal charcoal; litmus solution; lime-water; lead oxide; copper scale; soft coal; solution of quinine sulphate.

Apparatus. Lamp-stand; iron crucible; test-tubes; sealed tubes; beaker; funnel; filter-paper.

1. Heat bits of wood and paper in sealed tubes and note that the volatile gases burn. Also that something like water is given off which has an acid reaction toward litmus paper. What is left in the tube in each case? (503).

2. Fill the iron crucible half full of animal charcoal, cover with the iron plate, and support it on the medium ring of the lamp-stand without the wire gauze. Heat it as hot as possible for five minutes. Let it cool. This prepares what is known as "freshly ignited charcoal," to be used in some of the following experiments. While this is being done prepare some hydrogen sulphide water by passing the gas into water in a test-tube. Add some of the freshly ignited charcoal to the hydrogen sulphide water and shake the tube thoroughly. Note that the odor has been removed (504).

3. Boil 5 c.c. of the charcoal with 10 c.c. of litmus solution for two minutes and filter. Note that the color has been removed.

4. Shake a solution of quinine with some of the charcoal, filter, and taste the filtrate. Note that the bitter taste has been removed.

5. Make some impure water by mixing hydrogen sulphide water, quinine solution, and litmus solution. Add one quarter the bulk of freshly ignited charcoal, heat nearly to boiling with much stirring, and filter. Taste and smell the filtrate (504).

6. Place in a sealed tube an intimate mixture of finely divided charcoal and lead oxide. Connect the tube to a medium glass bend and heat as hot as possible, passing the evolved gases into a test-tube containing lime-water. What gas comes out of the tube? What must be left in the tube? (508).

7. Repeat with copper scale. What is left in the tube in this case?

8. Place some soft coal in a sealed tube and heat as hot as possible. What gas comes out of the tube? Will it burn? What is left in the tube? (505).

9. In Part III, write ten equations showing the reduction of ten different metallic oxides by means of carbon (508).

Questions on Exercise No. 26. Represent by equations all the reactions involved in this exercise. What are some of the products formed when wood and paper are heated in a sealed tube? (508). What classes of impurities does charcoal remove from solution? (504). How many liters of carbon dioxide, at normal pressure and temperature, would be produced if 100 g. of lead oxide were reduced to lead by charcoal? (253). What are some of the products formed when soft coal is heated in a sealed tube? (505). How is coke made? Write equations showing the reduction of metallic oxides with carbon.

LABORATORY EXERCISE NO. 27

Preparation and Properties of Carbon Dioxide (513–520)

Materials. Broken marble; powdered magnesite; charcoal in lumps; wood; magnesium wire; lime-water; sodium carbonate; sodium bicarbonate.

Apparatus. Lamp-stand; bottles; rubber stoppers; funnel-tube; wire gauze; evaporating-dish; combustion spoon.

1. Place a little lime-water in a large bottle. Balance a piece of charcoal on the combustion spoon. Ignite it by holding it in the flame, and lower into the bottle just over the lime-water. The carbon dioxide will produce a white precipitate of

calcium carbonate. Repeat in different bottles, burning wood and paper.

2. Place about 10 g. of powdered magnesite (MgCO₃) in a test-tube. Fit the tube with rubber stopper and delivery-tube. Heat the powder and pass the gas into a test-tube containing lime-water. What has the heat done to the magnesite? (517).

3. Place several pieces of broken marble in a 200-c.c. bottle, fit the bottle with two-hole rubber stopper, funnel-tube, and delivery-tube. Connect it with a wash-bottle, as shown in Fig. 25. Stand the generating-bottle on the lamp-stand with the funnel-tube through one of the rings to prevent the apparatus from being upset. Add dil. HCl through the funnel-tube and collect several bottles of the gas by upward displacement of air, testing with a burning splint to see when they are filled (517).
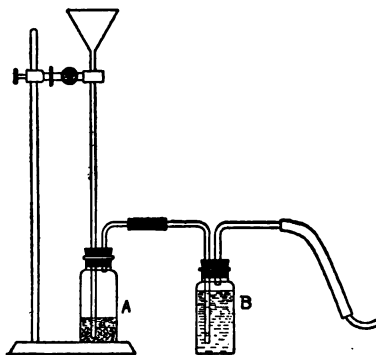
Fig. 25

4. Holding a piece of magnesium wire in the forceps, ignite it and thrust it down into a bottle partly filled with CO₂. What are the black specks? (515).

5. Run the delivery-tube to the bottom of a test-tube half filled with lime-water. Allow the gas to bubble through the lime-water until the precipitate which is first formed is entirely redissolved. This solution is known as "**water of temporary hardness**," for, if it be boiled, the excess of CO₂ will come out, and the lime, in the form of calcium carbonate, will be re-precipitated (678).

6. Remove the wash-bottle B from the apparatus, empty out the water, and place in it about 50 c.c. of lime-water. Blow in the long bend for a few moments and explain the result. Empty the product, add more lime-water, and connect the short bend to the suction-pump. Turn on the pump and note the time necessary to secure a precipitate. What does this show about the relative amount of CO₂ in the breath and in the air? (516).

7. Treat sodium carbonate with acids and represent the reactions by equations (517).

8. Heat some sodium bicarbonate in a test-tube and pass the evolved gas into lime-water.   What other product was formed here? (637).

9. Decant the liquid from the marble in the bottle A, wash the marble, and return it to the supply dish.   Boil down the liquid, or a portion of it, in the evaporating-dish on the gauze, and heat the residue until it is perfectly dry.   What is the residue?   Will it dissolve in water?   Does it absorb moisture? (671).

10. In Part III, write equations showing the decomposition of ten different carbonates, making use of ten different acids (82).

Questions on Exercise No. 27.   Represent by equations all of the reactions involved in this exercise.   What oxides does carbon form? (99). What oxide does it form when burned in an excess of oxygen?   How many grams of carbon would be necessary to form 22.4 liters of carbon dioxide at normal temperature and pressure? (253).   State three ways in which carbon dioxide may be prepared (517).   What acid does this oxide form with water? (515).   Is it stable or unstable?   What is the test for CO_2? (516).   What happens when an excess of CO_2 is passed into lime-water? What is water of temporary hardness? (678).   What is the first product formed when CO_2 is passed into sodium hydroxide?   What is the final product when an excess of the gas is used?   What is formed when sodium bicarbonate is heated? (637).   Describe some properties of calcium chloride (671).

LABORATORY EXERCISE No. 28

Acid Salts and Baking-Powder (530–535)

Materials.   Acid potassium tartrate; bicarbonate of soda; cornstarch; tartaric acid; normal potassium tartrate; limewater; dry sodium carbonate; broken marble.

Apparatus.   Lamp-stand; bottles; glass bends; rubber stoppers; rubber tube; beaker; test-tubes; large porcelain mortar.

Definitions.   A **polybasic acid** is one having more than one replaceable hydrogen.   Examples: H_3PO_4; H_2SO_4.

A **dibasic acid** is one having two replaceable hydrogens. Example: H_2SO_4.

A **tribasic acid** is one having three replaceable hydrogens. Example: H_3PO_4.

An **acid salt** is one formed by replacing part of the hydrogen of a polybasic acid by a basic radical. Examples: $HNaSO_4$; HNa_2PO_4.

A **normal salt** is formed by replacing all the hydrogens of a polybasic acid by the same kind of basic radical. Example: Na_2SO_4.

A **basic salt** may be considered as one formed by replacing only part of the oxygen of a basic oxide or part of the hydroxide of a base by an acid radical. Examples: $BiOCl$; $Bi(OH)_2NO_3$.

1. An acid salt may be made by adding an equivalent amount of acid or acid anhydride to a normal salt. Set up the carbon dioxide generator used in the previous experiment. Make a saturated solution of dry sodium carbonate in water. Add 5 c.c. of this solution to a test-tube, and allow a slow stream of CO_2 to bubble through it until there is a heavy precipitate. After the precipitate has formed filter it off, dry it by allowing it to stand, and prove that it is bicarbonate of soda (**637**). This will take some time. While this experiment is running proceed with the following:

2. Weigh out 10 g. of normal potassium tartrate, $K_2C_4H_4O_6$. From the following equation figure out the proper quantity of tartaric acid, and weigh it out (**252**):

$$K_2C_4H_4O_6 + H_2C_4H_4O_6 = 2\,HKC_4H_4O_6.$$

Dissolve each powder separately in 50 c.c. of hot water, and pour the normal salt solution into the acid solution in a bottle. The heavy white precipitate is bitartrate of potassium, acid potassium tartrate, or more commonly called **cream of tartar**. When it is cold filter it off by means of the suction-pump and filter-flask, wash it once or twice with water, and set it aside to dry. Taste it.

3. Baking-powders are mixtures of some kind of a pulverized acid or acid salt with bicarbonate of soda. They generally

contain some starch to keep the mixture dry. The best baking-powder is one made with cream of tartar. The equation representing its action when moistened is:

$$HNaCO_3 + HKC_4H_4O_6 = NaKC_4H_4O_6 + H_2O + CO_2.$$

From this equation calculate how much bicarbonate of soda should be used to go with 20 g. of cream of tartar. Weigh out the proper quantity. Mix these two powders very thoroughly in a large porcelain mortar or on a large sheet of paper. Add 5 g. of corn-starch and mix again. The more thoroughly it is mixed the better the powder will be (531).

Moisten a small quantity in a test-tube and explain the reaction.

4. In Part III, write four equations for other kinds of powders, using the following acids or acid salts: tartaric acid, acid potassium sulphate, acid calcium phosphate, $HCaPO_4$, and aluminum sulphate, $Al_2(SO_4)_3$. Aluminum sulphate is the commonest ingredient of cheap baking-powder. It reacts with the bicarbonate of soda to form sodium sulphate, aluminum oxide, and carbon dioxide (531).

Questions on Exercise No. 28. What is an acid salt? a basic salt? a normal salt? Give examples of each. What is a polybasic acid? a dibasic acid? a tribasic acid? Give examples of each. How may a normal salt be converted to an acid salt? How did you convert normal sodium carbonate to acid sodium carbonate? How did you prove that the product in 1 was acid sodium carbonate? (637). What is the essential composition of baking-powder? (530). Write equations showing the action of several kinds of baking-powder. Explain the fact that a solution of alum will decompose a carbonate (534). What salt is left in the cake when cream of tartar powder has been used? How many liters of CO_2, at normal pressure and temperature, could be produced by the action of 100 g. of cream of tartar acting on bicarbonate of soda? (252).

<center>LABORATORY EXERCISE No. 29</center>

<center>Silicon (545–556)</center>

Materials. Water-glass; sodium wire; barium chloride; cupric sulphate; sodium carbonate; lead oxide; hydrofluoric acid; cobalt nitrate.

Apparatus. Sealed tubes; evaporating-dish; mortar; square of cloth; scorifiers.

1. Place about 10 c.c. of water-glass in the mortar. **Do not measure it out.** Add about 5 c.c. of dil. HCl. Wash the jelly with water and strain it through a piece of cloth, allowing fresh water to run over the outside of the cloth during the straining. Transfer the material to the iron plate and heat it as hot as possible. This white material is silica. Is it an acidic or a basic oxide? (556). The following equation indicates the above reaction:

$$Na_4SiO_4 + 4\,HCl = 4\,NaCl + H_4SiO_4 \text{ (jelly)}.$$
$$H_4SiO_4 \text{ heated} = SiO_2 + 2\,H_2O.$$
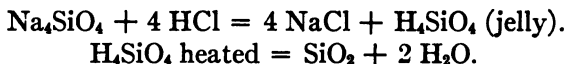
2. Grind the silica in the mortar. Test its solubility in HCl and in NaOH solution (555).

3. Place a minute amount of the powder in a sealed tube; on top of this place a bit of sodium wire. Cover the sodium with more of the powder and heat the whole as hot as possible. The sodium will extract the oxygen from the oxide and also from the glass, leaving black particles of silicon (549).

4. Break the tube by plunging it when hot into water in the evaporating-dish. Decant off the excess of water. Add sodium hydroxide solution to the residue and note whether or not it is possible to see bubbles coming from the black specks. The gas is hydrogen (547):

$$4\,NaOH + Si = Na_4SiO_4 + 2\,H_2.$$
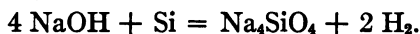
5. Dilute some water-glass with 5 times its bulk of water and divide into two parts. To one part add barium chloride solution and to the other cupric sulphate solution. What is the precipitate in each case?

6. The following equations represent the reactions involved in the making of a lead sodium glass (574):

$$Na_2O + PbO + 2\,SiO_2 = Na_2SiO_3 + PbSiO_3;$$
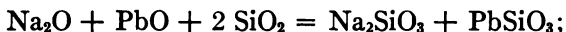
or, since the sodium oxide is usually added in the form of carbonate,

$$Na_2CO_3 + PbO + 2\,SiO_2 = Na_2SiO_3 + PbSiO_3 + CO_2.$$
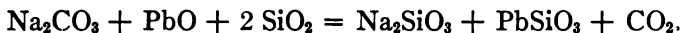
7. Weigh out and mix these things in the proportions called

for by the equation, making use of 1 g. of the silica you prepared in the first part of the exercise. Grind the whole in the mortar, adding a little water and a crystal of cobalt nitrate. Spread the plastic mixture over the inside of a small scorifier and heat to a white heat in the muffle-furnace. This will glaze the inside of the dish with a blue glass (568).

8. Warm a glass plate not hotter than can be borne by the hand. Cover one side thoroughly with beeswax and let the plate cool and the wax harden by itself. Make a drawing on the wax with any sharp point, being sure that the marks go through the wax. Cut two pieces of filter-paper just the size of the plate, place them on top of the waxed side and have them moistened with hydrofluoric acid. Leave the paper on the plate for five minutes, then remove it carefully, being particular not to get any of the acid on the hands. Wash the plate, warm it gently, and remove the wax with a towel.

The hydrofluoric acid has attacked the silica of the glass according to the following equation:

$$SiO_2 + 4\,HF = 2\,H_2O + SiF_4.$$
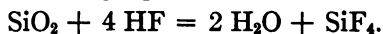
The SiF_4 is a gas (378).

Questions on Exercise No. 29. What is water-glass? (555). What reaction takes place when HCl is added to water-glass? If this jelly be heated, what is formed? What are the elements of the fourth group? What oxides do they form? Is silicon dioxide basic or acidic? What is the action of sodium on silicon dioxide? What acids does silicon form? (556). State three ways of dissolving sand (555). What is glass? (566). How is it made? (570). What is the action of hydrofluoric acid on silicon dioxide? (552). How many liters of silicon tetrafluoride could be formed by the action of hydrofluoric acid on 10 g. of silicon dioxide? (253). Represent all of the reactions involved in the above exercise by equations.

LABORATORY EXERCISE No. 30

Tin and Lead (591–621)

Materials. Granulated tin; stannous chloride solution; mercuric chloride solution; ammonium sulphide; strips of zinc; lead wire; lead nitrate solution; potassium chromate solution; H_2S.

Apparatus. Test-tubes; stopper and delivery-tube; lamp-stand.

1. Dissolve a small piece of tin in warm dilute hydrochloric acid. The gas given off is hydrogen. Fix the tube in clamp of lamp-stand with bottom of the tube near the base of the flame as in Fig. 21, and let the action continue for at least ten minutes. The solution contains stannous chloride, $SnCl_2$ (593).

2. To 1 c.c. of mercuric chloride solution add stannous chloride from reagent bottle drop by drop, until no further change takes place. The white precipitate that forms at first is mercurous chloride, HgCl. The final gray precipitate is metallic mercury. The stannous chloride is changed to stannic chloride, $SnCl_4$, which remains in solution. Write two equations (593).

3. Repeat this test with the stannous chloride which you have made.

4. To 2 c.c. of stannous chloride solution add 5 c.c. of water, and then hydrogen sulphide. Filter off the precipitate. Stand the funnel in a clean test-tube and add a little yellow ammonium sulphide to the filter. Yellow ammonium sulphide contains an excess of sulphur dissolved in it. The brown sulphide dissolves because it forms with the yellow ammonium sulphide a soluble compound known as ammonium thiostannate, $(NH_4)_2SnS_3$ (593). This runs through the filter into the test-tube. Add some hydrochloric acid to this solution. The following reaction takes place:

$$(NH_4)_2SnS_3 + 2\,HCl = 2\,NH_4Cl + H_2S + \underline{SnS_2}.$$
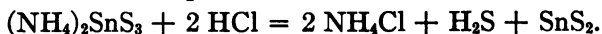
5. To 2 c.c. of stannous chloride solution add 10 drops of concentrated nitric acid, and heat gently. This oxidizes the stannous chloride solution to stannic chloride. Represent by equation.

Remember that this solution contains an excess of free hydrochloric acid (145). Dilute with 10 c.c. of water and pass in hydrogen sulphide. The precipitate is stannic sulphide. Filter it off and treat it just as you did the stannous sulphide.

6. Place about 5 c.c. of stannous chloride solution from reagent bottle in test-tube and add a strip of zinc (196).

7. Examine a piece of lead wire. Try to dissolve it in sulphuric, hydrochloric, and hot dilute nitric acid (601).

8. Test a solution of lead nitrate with sulphuric acid and

with potassium chromate solution. Pass hydrogen sulphide into a very dilute solution of lead nitrate (603).

9. To 2 c.c. of lead nitrate solution add one drop of sodium hydroxide solution. Now add an excess of sodium hydroxide. Compare the corresponding reaction with tin.

10. To 5 c.c. of lead nitrate solution in test-tube add a strip of zinc. Leave it for at least ten minutes (196).

Questions on Exercise No. 30. Represent by equations all the reactions involved in this exercise. What are the elements of the fourth group? What oxides do tin and lead form? (99). Are these oxides basic or acidic? What acids does tin form? (593). What salt is formed when tin is dissolved in hydrochloric acid? How many liters of hydrogen would be formed if 10 g. of tin were dissolved? (253). Explain the changes that take place when stannous chloride is gradually added to a solution of mercuric chloride. What is the color of stannous sulphide? When this is dissolved in yellow ammonium sulphide what compound is formed? (593). When this solution is acidified with hydrochloric acid what is the precipitate? What is the color of stannic sulphide? How could you change stannous sulphide to stannic sulphide? Explain the effect of adding a piece of zinc to a solution of stannous chloride (196). What will dissolve lead? In what acids will it not dissolve? Describe lead sulphide, lead sulphate, lead chromate. How many grams of zinc would precipitate 10 g. of lead from solution? How many grams of lead would produce 10 liters of nitric oxide? (253).

LABORATORY EXERCISE No. 31

Sodium and Potassium (622–656)

Materials. Sodium bicarbonate; lime-water; sodium carbonate; sodium chloride; calcium chloride; barium chloride; sodium nitrate; sodium sulphate; potassium chloride; hydrogen potassium tartrate; potassium nitrate; potassium sulphate.

Apparatus. Test-tubes; stopper and delivery-tube; iron wire with loop on end; glass plate; beaker; wire gauze; lamp-stand; copper wire; square of blue glass.

1. Shake up a teaspoonful of common salt in a bottle with a test-tube full of strong ammonia. Filter off ½ t.t. of the solution. Pass carbon dioxide through the solution for about an hour. Set the tube away until the next laboratory ex-

ercise. The precipitate is sodium bicarbonate, made by the **ammonia,** or **Solvay, process.** Filter it off and prove that it is bicarbonate (634).

2. Heat 5 c.c. of bicarbonate of soda in a test-tube having a delivery-tube that passes into lime-water. **Do not melt the tube.** What is left in the tube? When the tube is cold add 2 or 3 c.c. of cold water. Explain the evolution of heat (637).

3. Dissolve a very small quantity of common salt in water and let some of the solution evaporate on a glass plate. Examine the crystals under the microscope (631).

4. Add some calcium chloride solution, also some barium chloride solution, to separate portions of sodium carbonate solution.

5. Clean an iron wire by dipping it repeatedly in a test-tube containing concentrated hydrochloric acid, washing, and heating, until it gives no color when heated in the Bunsen flame. Moisten it with water, touch it to some sodium salt, and heat in the Bunsen flame. What color does sodium impart to the flame? Observe this color through the blue glass (625).

6. Dissolve 8 g. of potassium chloride and 10 g. of sodium nitrate in 20 c.c. of water in beaker on wire gauze on lamp-stand, and boil off half of the water. Let the precipitate settle and pour the liquid off into a test-tube. Dissolve a very small quantity of the residue in water and let a few drops of the solution evaporate on a square of glass. Examine the crystals under the microscope. What are they? Allow the tube containing the liquid to stand until cold. Crystals will form. What must they be? (652).

7. Test compounds of potassium in the flame just as you did the sodium. Note the color through the blue glass. Put both compounds of sodium and potassium on the wire at once and note the flame color without and with the blue glass. Which color predominates without the glass? Which with it? (648).

Questions on Exercise No. 31. What are the elements of the first group? What oxides do these elements form? Are they basic or acidic? (96). Represent by equations all the reactions involved in this exercise. What reactions are involved in the Solvay process? (634). How would you form calcium and barium carbonates? How do sodium and

potassium color the Bunsen flame? Which color would obscure the other? How is it possible to see the potassium color in the presence of sodium? How is potassium nitrate made? How many grams of bicarbonate of soda would be necessary to give 10 liters of carbon dioxide when heated? (253).

LABORATORY EXERCISE No. 32

Calcium, Strontium, and Barium (661–692)

Materials. Quicklime in lumps; sodium carbonate; strontium nitrate; barium chloride solution; calcium chloride.

Apparatus. Lamp-stand; beaker; wire gauze; test-tubes; iron wire; flask.

1. Heat ½ t.t. of water to boiling in beaker on wire gauze. Add a lump of lime half the size of an egg. The lime ought to crumble to a white, dry, amorphous powder (669). This is **dry-slacked lime,** or **calcium hydroxide, $Ca(OH)_2$.**

2. Add water and stir to the consistency of milk. This is **"milk of lime,"** or whitewash. Dilute a portion of this very much with water, and filter. Feel the filtrate with the fingers, test it with litmus paper, and taste it. It is a very dilute solution of calcium hydroxide and is known as **lime-water.** Do you consider calcium hydroxide very soluble? (669).

3. Dissolve about 4 g. of sodium carbonate in boiling water in flask and add a tablespoonful of milk of lime. Stir thoroughly and filter. Feel the filtrate with the fingers. Test it with litmus paper. What is it? What remained on the filter? (639).

4. Dissolve some milk of lime in hydrochloric acid and test the product on iron wire in the flame. Add sodium carbonate solution to some calcium nitrate solution.

5. Make some strontium nitrate solution and add some sodium carbonate solution. To another portion add some sulphuric acid. Test some of the dry salt moistened with HCl in the flame.

6. Repeat these tests with barium chloride. How could you distinguish between barium and strontium?

Questions on Exercise No. 32. Name the elements in the second group. What oxides do they form? Are these oxides basic or acidic?

(97). Represent by equations all the reactions involved in this exercise. Name the alkaline earth metals. Describe the appearance of calcium hydroxide. How is lime made? (668). How soluble is calcium hydroxide? What is lime-water and how is it made? How is sodium hydroxide made? How did you make calcium carbonate? How did you make strontium sulphate? How do calcium compounds color the flame? How could you distinguish between a calcium and a strontium compound? A hydrochloric acid solution contains 20 per cent acid and has a specific gravity of 1.1; how many cubic centimeters of such a solution would be necessary to dissolve 10 g. of calcium hydroxide? (256).

LABORATORY EXERCISE No. 33

Magnesium, Zinc, Cadmium, and Mercury (698–737)

Materials. Magnesium wire; hydrogen disodium phosphate; granulated zinc; ammonium sulphide; cadmium sulphate; strips of zinc; mercury; mercuric chloride; hydrogen sulphide; brass.

Apparatus. Bottle; evaporating-dish; test-tubes.

1. Burn some magnesium wire in a bottle. Don't drop the burning wire into the bottle, but hold it in the forceps while burning. Shake the product with water and test with litmus paper. Is magnesium oxide basic or acidic? What is formed when it is dissolved in water? (705).

2. Add magnesium wire to 2 or 3 c.c. of dilute hydrochloric acid in porcelain dish until no more will dissolve. Dilute the solution. What does it contain? To a portion of this solution add ammonium hydroxide. What is the precipitate? (706).

3. To another portion add 10 c.c. of hydrochloric acid and an excess of ammonia. What compound is present here which prevents the precipitation of magnesium hydroxide? (706).

4. To this same solution add a few drops of hydrogen disodium phosphate. The precipitate is ammonium magnesium phosphate, NH_4MgPO_4. This is the common test for magnesium (701).

5. Make a careful test to see if hydrogen is given off when magnesium is boiled with water containing ammonium chloride.

6. Dissolve about 1 g. of zinc in 5 c.c. of dil. nitric acid. What have you in solution? Represent the reaction by an

equation. What gas was given off? Dilute the solution (**713**).

7. To a portion of this solution add sodium hydroxide drop by drop until a precipitate is formed. What is the precipitate? (**714**). Then add an excess of the hydroxide. Why does the precipitate dissolve? Toward a strong acid zinc hydroxide acts like a base; toward a strong base it acts like an acid, having the formula H_2ZnO_2. What soluble compound is formed when zinc hydroxide dissolves in sodium hydroxide? What other hydroxides act like zinc hydroxide in this respect? (**802**).

8. Pass hydrogen sulphide into 10 c.c. of ammonia in a test-tube for five minutes. What compound is formed? (**396**). Add this solution to a small quantity of the zinc solution. What is the precipitate? Is this precipitate soluble in dilute hydrochloric acid? (**714**). Is copper sulphide soluble in dilute hydrochloric acid? How could you separate zinc and copper? Dissolve a very small piece of brass and prove that it contains both zinc and copper.

9. Find out what cadmium sulphide is like and whether it is soluble in dilute acids (**720**).

10. Dissolve a very small globule of mercury in 2 or 3 c.c. of hot dilute nitric acid. Dilute the solution. Pass hydrogen sulphide into a portion of the solution and dip a bright piece of copper wire into another portion. The solution contains mercuric nitrate (**727**).

11. Cover a small globule of mercury with cold dilute nitric acid and let it stand until the next laboratory exercise. This solution will contain mercurous nitrate, $HgNO_3$. To a portion of it add a few drops of hydrochloric acid. What other chlorides are insoluble? Filter off the precipitate and add ammonia to the filter (**731**).

Questions on Exercise No. 33. Represent by equations all the reactions involved in this exercise. What oxide does magnesium form? Is it basic or acidic? What is formed when it dissolves in water? How many cubic centimeters of a hydrochloric acid solution having a specific gravity of 1.1 and containing 20 per cent acid would be necessary to form 10 liters of hydrogen when acting on a metal? (**256**). What precipitate is formed when ammonium hydroxide is added to a solution of magnesium chloride? (**706**). What is the nature of the action of dilute nitric acid on zinc? What is the precipitate that is formed at first when sodium hy-

droxide acts on a solution of a zinc salt? Has this precipitate any acid properties? Why does it dissolve when an excess of sodium hydroxide is added? What compound is formed? How could you separate zinc and copper by means of hydrogen sulphide? What is the color of cadmium sulphide? What two nitrates does mercury form and under what circumstances would each result?

LABORATORY EXERCISE NO. 34

Copper and Silver (738–772)

Materials. Copper wire; silver foil; iron wire; blue vitriol; grape-sugar solution; cupric sulphate solution; potassium iodide solution; silver nitrate solution; sodium chloride.

Apparatus. Test-tubes.

1. Place about 1 in. of dil. HNO_3 in test-tube and add as much copper wire as it will dissolve. Do this in the hood. Describe and explain the reaction (**741**).

2. Divide the solution into two parts. Heat one of these and add ammonia little by little, with much shaking, until the precipitate formed at first redissolves completely. Stand the tube in the rack until the next laboratory exercise. Beautiful blue crystals of cupro-ammonium nitrate will be found. Formula, $Cu(NO_3)_2 \cdot 4 NH_3$ (**742**).

3. Dilute the other portion with water. Pass hydrogen sulphide into a portion of this solution diluted with water (**742**). Pass hydrogen sulphide into some very dilute cupric sulphate solution. See if it is possible to remove all the copper from solution in this way. Heat some blue vitriol in a sealed tube and note the change in the color. Allow some of the water to run back on the anhydrous material (**752**).

To 5 c.c. of grape-sugar solution in test-tube add 5 c.c. of cupric sulphate solution. Now add sodium hydroxide solution, shaking until the precipitate first formed is redissolved.

Warm carefully, noting the changes. Let it stand. The precipitate is cuprous oxide. The grape-sugar acted as a reducing agent; do not attempt to make use of its formula in your equation (**749**).

4. Put a piece of iron wire into some cupric sulphate solution (**196**).

5. Add some sodium hydroxide solution to some cupric sulphate solution. Heat to boiling. The precipitate first formed is cupric hydroxide. When it is heated each molecule gives up one molecule of water. What is the black precipitate you finally obtain? Solutions of salts of many other heavy metals behave in the same way (**751**).

6. To a small portion of some copper solution add ammonium hydroxide little by little at first, and finally in excess. This intense color is quite characteristic of copper (**742**).

7. Dissolve a piece of silver-foil in about 1 in. of dilute nitric acid. Describe the reaction and write the equation. Add water to half-fill the tube and explain later why this makes the solution cloudy (**756**).

8. To 2 c.c. of this solution add a solution of sodium chloride. Boil the contents of the tube (**756**). Get the precipitate on a filter and expose it to sunlight. To another portion add a piece of copper wire (**196**).

9. To 1 c.c. of silver nitrate solution add a little potassium iodide solution. Pass hydrogen sulphide through a very dilute solution of silver nitrate.

10. Devise a method for testing for silver, lead, and mercurous mercury contained in the same solution (**756**).

Questions on Exercise No. 34. Write the equation for the action of dil. HNO_3 on copper. Is nitric oxide always given off when nitric acid acts on a metal? (**741**). What is the first visible effect of adding ammonium hydroxide to a copper nitrate solution? (**742**). What happens when an excess of ammonia is added? What two oxides does copper form? (**96**). How did you make cuprous oxide in the laboratory? What is the formula for blue vitriol? What happens when blue vitriol is heated? How did you make cupric oxide? (**751**). State three general methods for the preparation of metallic oxides. (Chapter XXXVIII.) Why does iron precipitate copper from solution? (**196**). What is the most striking reaction of copper compounds? What is the nature of the action of nitric acid upon silver? How could you distinguish between silver and lead chlorides? (**756**). How could you separate silver, lead, and mercurous mercury if they were all present in the same solution? (**756**). How many cubic centimeters of HCl solution having a specific gravity of 1.1 and containing 20 per cent acid would be necessary to precipitate all the silver in 100 c.c. of a silver nitrate solution having a specific gravity of 1.01 and containing 1 per cent silver nitrate? (**256**).

LABORATORY EXERCISE No. 35

Iron and Manganese (773–799)

Materials. Green vitriol; fine iron wire; chlorine water; potassium nitrate; red lead; ammonium sulphate; carbon dioxide; cupric sulphate solution; potassium ferrocyanide solution; ammonium thiocyanate; potassium ferricyanide; manganese dioxide; sodium nitrite; potassium hydroxide; potassium permanganate; sulphurous acid.

Apparatus. Flask; lamp-stand; wire gauze; test-tubes; beaker; evaporating-dish; iron crucible.

1. Place 40 c.c. of water in the flask, add 10 c.c. of conc. sulphuric acid, and mix the liquids by shaking. Weigh out about 10 g. of fine iron wire and place it in the dilute acid. Heat the flask on the lamp until the reaction will proceed by itself, then stand the flask in the hood until all the iron is dissolved. Filter the hot solution and divide the filtrate into two portions. Set one portion aside to crystallize and dilute the other for use in the following experiments (796).

2. Test the action of the dilute and concentrated cold and hot acids on bits of iron wire.

3. To a few drops of ferrous sulphate solution from 1 add a little ammonium hydroxide solution. The precipitate is ferrous hydroxide. Watch it for some time and explain what happens to it (791). Add concentrated nitric acid until the precipitate dissolves, then boil. Cool, and again make alkaline with ammonia. What did the nitric acid do to the ferrous sulphate solution? (144).

4. Make a little ferrous chloride solution by dissolving iron wire in hydrochloric acid, and add chlorine water in excess. An excess is present if an odor of chlorine remains after warming. Add ammonium hydroxide and explain result. What did the chlorine water do to the ferrous chloride? (145).

5. To a few drops of ferric chloride solution add ammonium hydroxide. Note the color of the precipitate. It is ferric hydroxide (792). Dissolve it in hydrochloric acid and add a bundle of fine iron wire. Heat to boiling from time to time

for three minutes. Pour some of the almost colorless solution into hot ammonia. What is the precipitate? And what did the iron wire do to the ferric chloride? (**792**).

6. Add a few drops of ammonium sulphide to a little ferrous sulphate solution. To a little ferric chloride solution add ammonium sulphide and acidify with hydrochloric acid. What is the undissolved residue? Make the solution alkaline with ammonium hydroxide and explain what the ammonium sulphide must have done to the ferric chloride (**792**).

7. Dissolve 20 g. of green vitriol (crystallized ferrous sulphate, $FeSO_4 + 7 H_2O$), and the proper quantity of ammonium sulphate to make ferrous ammonium sulphate, $(NH_4)_2SO_4.FeSO_4 + 6 H_2O$, in 50 c.c. of water, boiling, in flask, and filter into bottle. Set aside to crystallize. How should you test these crystals for iron, ammonium, and for sulphate? (**798**).

8. Test both ferrous and ferric iron solutions with each of the following reagents and tabulate the results: Potassium ferrocyanide, potassium ferricyanide, and ammonium thiocyanate. Devise a method for testing for ferrous and ferric iron, each in the presence of the other (**791, 792, 793**).

9. What is the action of ammonium hydroxide, also of ammonium sulphide, on potassium ferrocyanide solution? Explain.

10. Heat a small quantity of manganese dioxide in a sealed tube. What gas is given off, and what is left in the tube? Heat $\frac{1}{4}$ g. of manganese dioxide in a test-tube with 5 c.c. of conc. HCl. What gas is given off? What kind of a reaction is this? (**778**).

11. Shake up some manganese dioxide with a strong solution of sulphur dioxide in water. Add a small piece of sodium nitrite to a tube containing $\frac{1}{4}$ g. of manganese dioxide and 5 c.c. of dilute nitric acid. Heat to boiling. Add $\frac{1}{2}$ g. of red lead. Some of the manganese is oxidized to permanganic acid.

12. Fuse 1 g. of manganese dioxide with 1 g. of potassium hydroxide and a small quantity of KNO_3, in iron crucible. Dissolve out the product with water, filter, and pass carbon dioxide into the solution. Potassium permanganate is formed in solution (**775**).

13. Dilute some of the ferrous sulphate solution with water, and add potassium permanganate solution (**144**).

Questions on Exercise No. 35. How did you make ferrous sulphate? How else might you have made it? What is the formula of green vitriol? (**796**). What acids dissolve iron and under what conditions? Describe ferrous hydroxide (**791**). If an oxidizing agent be added to a ferrous iron solution, what kind of change takes place? (**144**). Describe ferric hydroxide (**792**). How could you change ferric hydroxide to ferrous chloride? What is the effect of adding ammonium sulphide to a ferrous solution? to a ferric solution? (**791–792**). How did you make ferrous ammonium sulphate? (**798**). Describe how to test for both ferrous and ferric ions in the presence of each other (**793**). Why do not solutions of potassium ferrocyanide react for iron ions with ammonium hydroxide? What is the effect of heating manganese dioxide? (**778**). Write the equation for the action of conc. HCl on MnO_2. What is the visible effect of shaking MnO_2 powder with sulphurous acid? (**778**). How could you convert MnO_2 to a solution of permanganic acid? How is potassium permanganate made? What is the action of potassium permanganate solution on ferrous sulphate solution, containing some sulphuric acid? (**144**). Write the equation for the above reaction.

LABORATORY EXERCISE No. 36

Aluminum and Chromium (800–819)

Materials. Aluminum wire and foil; alum; borax; sodium carbonate; aluminum sulphate; ammonium sulphate; ammonium sulphide; chrome-alum; potassium chromate; alcohol; lead nitrate; barium chloride; silver nitrate; mercuric chloride solution.

Apparatus. Lamp-stand; bottles; test-tubes; evaporating-dish; beaker; wire gauze.

1. Test the solubility of aluminum in nitric, hydrochloric, and sulphuric acids, both dilute and concentrated, also in sodium hydroxide solution. Evaporate the solution of aluminum chloride you have made to dryness in the hood. Heat the residue. When it has cooled try to dissolve it in water (**802**).

2. Amalgamate a strip of aluminum foil in mercuric chloride solution, allowing the reaction to continue for several minutes. Wipe off the solution with clean filter-paper (**196**).

After a time notice the remarkable change it has undergone and feel it to note the heat of reaction.

3. To an alum solution add ammonium hydroxide solution until sufficient is present to dissolve the precipitate which first forms. Boil a little of this clear solution. The hydroxide is reprecipitated. This is the regular test for the aluminum radical in solution (803).

4. Put a little alum solution in each of three test-tubes. Add borax solution to one, sodium carbonate solution to another, and sodium hydroxide to the third. Compare the results and explain (250).

5. Take 10 g. of aluminum sulphate and the required quantity of ammonium sulphate to make ammonium alum. Dissolve the two salts together in 50 c.c. of boiling water. Filter the solution into a bottle and set aside to crystallize. After several days crystals of ammonium alum will be found. Formula, $(NH_4)_2SO_4 . Al_2(SO_4)_3 + 24 H_2O$. Get these out, dissolve them in water, and test the solution for ammonium, sulphate, and aluminum radicals (812).

6. Add a few drops of ammonium sulphide to an alum solution. Filter off the precipitate and test it for a sulphide (250).

7. Add ammonium hydroxide to a little chrome-alum solution. Compare the precipitate with that formed by treating common alum in the same way. Treat another portion of chrome-alum solution with sodium hydroxide and observe its action with an excess of the precipitant (814).

8. Precipitate chromic hydroxide with sodium hydroxide and then add enough of the latter to redissolve the precipitate. Dilute the solution with an equal volume of water and then pour away all but about an inch in a test-tube of the solution. Add about 5 g. of chloride of lime and boil for several minutes until the solution is quite yellow. Filter into a test-tube and acidify the filtrate with hydrochloric acid. Note and explain the successive color changes.

9. Dissolve 10 g. of potassium bichromate in 50 c.c. of water in flask. When solution is complete add 10 c.c. of conc. sulphuric acid. Transfer a few drops to a test-tube and add ammonia. To the rest of the solution, under the hood, add 5 c.c. of alcohol. The mixture of sulphuric acid and potassium bichromate oxidizes the alcohol to aldehyde (C_2H_4O), which

has a strong irritating odor. Add ammonia to a few drops of this solution in a test-tube. Leave the rest of the solution in a bottle to crystallize (819).

10. Test potassium bichromate solution with lead nitrate, barium chloride, and with silver nitrate (819).

Questions on Exercise No. 36. What oxides do aluminum and chromium form? (98). What reagents will dissolve aluminum? (802). Write the equations. Is aluminum very basic? (802). Does aluminum hydroxide ever act as an acid? (802). What is the general nature of an alum? (812). Give the formulas of several alums. How do aluminum salts in solution act toward litmus paper? (250). How could you change basic chromium to acid chromium? Describe the changes which take place when alcohol is added to a solution of potassium dichromate and sulphuric acid? What salt will crystallize from the above mixture? (817). How many cubic centimeters of a potassium dichromate solution having a specific gravity of 1.03 and containing 5 per cent of the salt would be necessary to oxidize all the iron in 100 c.c. of a ferrous sulphate solution having a specific gravity of 1.05 and containing 10 per cent of green vitriol? (256). Give the formulas of ten oxidizing agents and state how they oxidize (115).

LABORATORY EXERCISE No. 37

REVIEW LABORATORY WORK

I. The Identification of Common Chemical Compounds
Preliminary Examination

1. If it is a solid, pulverize it and put it in a bottle or tube marked with its letter or number.
2. If you recognize it or think you do, make the final confirmatory tests as called for in these directions at once.
3. Test its action toward moist litmus paper.
   (a) Turns red; shows an acid anhydride, acid, or acid salt, or salt of a strong acid with weak base.
   (b) Turns blue; shows an alkali, an alkaline oxide, or an alkaline carbonate or alkaline salt of weak acid.
4. Heat a small portion in a sealed tube as hot as possible.
   (a) There may be no change, possibly a sulphate.
   (b) It may give off water, showing water of crystallization or water of decomposition.

(c) It may give off a colorless gas which turns lime-water white, showing a carbonate or bicarbonate.

(d) It may give off red fumes, showing a nitrate or nitrite.

(e) It may leave a black residue of carbon, showing it to be an organic compound.

(f) It may simply melt, showing nothing.

(g) It may give a sublimate of sulphur, showing it to be a thiosulphate.

(h) It may volatilize completely, showing it to be either ammonium nitrate or ammonium carbonate.

(i) It may sublime completely, showing it to be an ammonium compound or a mercury compound.

(j) The substance may be yellow when hot and white when cold, showing it to be a zinc compound.

5. Moisten a small quantity of the solid with dil. HCl.

(a) Effervescence of a colorless gas that turns lime-water white shows a carbonate or bicarbonate.

(b) Effervescence of a colorless gas that smells of sulphur dioxide shows a sulphite or a thiosulphate.

(c) Odor of hydrogen sulphide shows presence of a sulphide.

(d) Odor of chlorine shows the substance to be an oxidizing agent.

6. Clean the iron-wire loop by dipping it in a test-tube of hot dilute hydrochloric acid, washing and heating until it does not color the flame. Moisten a very small quantity of the powder on a glass plate with conc. HCl. Place a small quantity of this mixture on the clean end of the wire and heat it carefully in the edge of the flame.

(a) Yellow color shows sodium. **Remember that sodium is almost always present in small quantities as an impurity.** Yellow flames should always be examined through the blue glass. A red color when seen through the blue glass shows potassium.

(b) A purple color appearing red through the blue glass shows potassium. The blue glass removes the yellow color due to sodium which might obscure the purple.

(c) Red color without the glass shows lithium, calcium, or strontium.

(d) Green color shows barium or copper.

7. Heat about 3 g. of the dry powder in a test-tube with 3 drops of water and 3 c.c. of conc. sulphuric acid.

(a) No change; possibly a sulphate.

(b) Evolution of hydrochloric acid gas; a chloride.

(c) Evolution of nitric acid, a colorless liquid distilling up on the sides of the tube, shows a nitrate.

(d) Evolution of sulphur dioxide without the formation of sulphur shows a sulphite.

(e) Evolution of sulphur dioxide with the formation of sulphur shows a thiosulphate.

(f) Bromine distilling up the sides of the tube accompanied by acid fumes shows a bromide.

(g) A purple vapor shows an iodide.

(h) Evolution of an acid gas that etches the inside of the tube shows a fluoride.

(i) Odor of vinegar shows an acetate.

8. Add a small quantity of sodium hydroxide solution to 2 g. of the dry material in the mortar. Mix thoroughly with the pestle. The odor of ammonia shows an ammonium compound.

9. If the material is an acid or an acid anhydride, it will unite readily with sodium hydroxide solution to form a salt with the evolution of much heat.

10. If the material is a base or a basic oxide, it will unite readily with dilute nitric acid to form the corresponding salt with the evolution of much heat.

The above preliminary tests should have given some indication as to the nature of the substance. In case they have, proceed at once to make the final confirmatory tests for the radicals whose presence is suspected. If they have not, the next step is to make a solution of about 5 g. of the material either in water or dilute nitric acid. Make up the solution to 100 c.c. and use small portions of it in the following tests.

Wherever a definite reaction is obtained leave a blank line in the note-book to be filled in later with an equation repre-

senting that reaction, when the nature of the substance is definitely known.

II. Tests to Be Made with a Water or Nitric Acid Solution of the Material

These tests must invariably be made in the order given.

1. Add a few drops of dil. HCl to a small portion of the solution.
   (a) A white precipitate shows silver, lead, or mercurous mercury.
2. Pass H_2S through a small quantity of the solution, to which a few drops of hydrochloric acid have been added if it was not already an acid solution.
   (a) A black precipitate shows lead, copper, bismuth, or mercuric mercury.
   (b) A light-yellow precipitate shows cadmium or arsenic.
   (c) An orange-yellow precipitate shows antimony.
3. Make alkaline with ammonia, and pass H_2S through the liquid.
   (a) A black precipitate shows nickel, cobalt, or iron.
   (b) A pink precipitate shows manganese.
   (c) A white precipitate shows zinc.
4. Add ammonia and heat to boiling.
   (a) A white gelatinous precipitate shows aluminum, bismuth, magnesium, or a phosphate.
   (b) A brown gelatinous precipitate shows ferric iron.
5. Add a solution of sodium carbonate.
   (a) A white precipitate shows calcium, strontium, barium, or magnesium.
6. To a small portion of the water solution add silver nitrate.
   (a) A white precipitate shows a chloride, nitrite, or thiosulphate.
   (b) A cream-colored precipitate shows a bromide.
   (c) A light-yellow precipitate shows an iodide.
   (d) A bright-yellow precipitate shows a phosphate.
   (e) A deep-red precipitate shows a chromate.
7. To a nitric acid solution, or solution to which a few drops of nitric acid have been added, add silver nitrate.

(a) White precipitate soluble in ammonia shows a chloride.

(b) Cream-colored precipitate shows a bromide.

(c) Light-yellow precipitate shows an iodide.

8. Add barium chloride solution.

    (a) White precipitate soluble in dil. HCl shows a phosphate or carbonate.

    (b) White precipitate insoluble in dil. HCl shows a sulphate.

    (c) Light-yellow precipitate shows a chromate.

III. Confirmatory Tests

In each of these tests use small portions of a water or nitric acid solution.

Lead. With HCl, white precipitate soluble in hot water; with potassium dichromate, yellow precipitate; with H₂S, black precipitate; with sheet zinc, black precipitate of metallic lead.

Silver. With HCl, white curdy precipitate soluble in ammonia; with H₂S, black precipitate; with copper, white precipitate of metallic silver.

Mercurous mercury. With HCl, white precipitate that is blackened with ammonia; with H₂S, black precipitate; covers bright copper wire with mercury.

Copper. With excess of ammonia, deep-blue solution; H₂S, black precipitate; deposits copper on bright iron wire; boiled with excess of sodium hydroxide gives black precipitate of cupric oxide.

Mercuric mercury. With stannous chloride gives at first a white precipitate which turns gray on adding an excess; with H₂S, black precipitate; deposits mercury on bright copper wire.

Bismuth. White gelatinous precipitate with ammonium hydroxide. If this precipitate be collected on a filter and a solution of stannous chloride in sodium hydroxide be added to it, it will be blackened.

Cadmium. With hydrogen sulphide gives a yellow precipitate; with sodium hydroxide a white gelatinous precipitate.

Antimony. With hydrogen sulphide an orange-yellow precipitate of antimony trisulphide, completely soluble in yellow ammonium sulphide.

Ferrous iron. With ammonia a light-green precipitate which rapidly turns brown on the surface; with potassium ferricyanide a deep-blue precipitate.

Ferric iron. With potassium or ammonium thiocyanate a deep-red solution; with ammonium hydroxide a brown gelatinous precipitate; with potassium ferrocyanide deep-blue precipitate.

Aluminum. With ammonia, white gelatinous precipitate soluble in excess of ammonia, insoluble in boiling ammonia.

Basic chromium. When treated with chloride of lime, or sodium oxychloride and sodium hydroxide it is oxidized to chromate and recognized by its yellow color.

Zinc. Hydrogen sulphide passed into ammonia and the solution added to a neutral solution of a zinc salt gives a white precipitate of zinc sulphide.

Ammonium hydroxide gives a white precipitate of zinc hydroxide easily soluble in an excess of ammonia.

Nickel. Sodium hydroxide gives an apple-green precipitate insoluble in excess of sodium hydroxide.

Manganese. Fused with a small quantity of sodium carbonate and potassium nitrate on platinum foil over blowpipe gives a green color.

Magnesium. Ammonium hydroxide gives a white precipitate of magnesium hydroxide soluble in excess of HCl, from which solution it is not reprecipitated by ammonia. Sodium phosphate added to this solution gives a white precipitate of ammonium magnesium phosphate.

Barium. White precipitate with K_2SO_4 insoluble in HCl. Yellow precipitate with potassium chromate. Green flame coloration.

Strontium. Red flame coloration. White precipitate with potassium sulphate.

Calcium. Yellowish-red flame coloration. No precipitate in very dilute solution with K_2SO_4; white precipitate with Na_2CO_3 solution.

Sodium. Bright-yellow flame coloration.

Potassium. Violet flame coloration which appears red through a blue glass. The sodium color obscures the potassium color, therefore all yellow colors must be examined through the blue glass.

Ammonium. Grind about 2 g. of the material in the mortar with sodium hydroxide solution, and smell for ammonia.

Chloride. Silver nitrate gives a white curdy precipitate insoluble in dilute nitric acid and soluble in ammonia.

Bromide. Silver nitrate gives a cream-colored precipitate insoluble in dilute nitric acid. The original solution treated with a few drops of concentrated nitric acid and shaken with a little carbon disulphide gives a yellow or a red globule.

<div align="center">

LABORATORY EXERCISE NO. 38

The Preparation of Chemical Compounds

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This exercise is intended for the more advanced student who is enthusiastic about the work and is anxious to make some compounds on a large scale. It seems as though such a student should be able to study out the details for such work by himself with the help of a few general directions, supplemented, if necessary, by reference to the literature on the subject. When he knows exactly what he desires to make and every detail necessary to produce the result, he should be provided with the necessary materials and apparatus.

General Directions for Making Chemical Preparations

Acids. 1. Volatile and stable acids may be made by distilling a salt of the desired acid with the proper quantity of

Fig. 26

sulphuric acid in a glass retort and condensing or absorbing the distillate (Fig. 26). HNO_3, HCl, H_2S, HF, $HC_2H_3O_2$ (82).
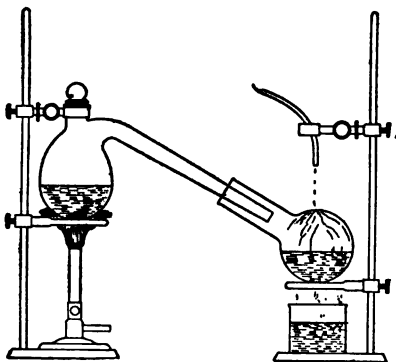
2. Oxygen acids may be prepared by dissolving the acid anhydride in water and concentrating if necessary. H_2SO_4, H_3PO_4, H_2CO_3, H_2SO_3, HIO_3, H_2CrO_4 (101).
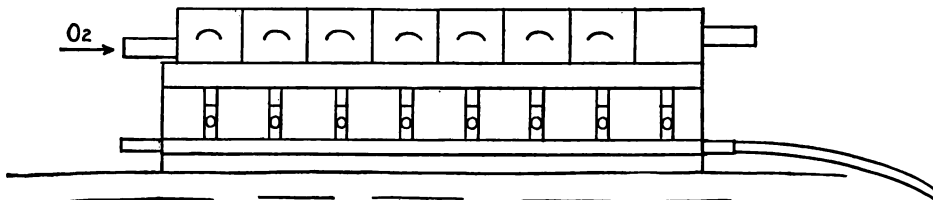
FIG. 27

3. Oxygen acids may also be prepared by oxidizing the acid-producing element directly by nitric acid. H_3PO_4, H_3AsO_4, H_3SbO_4, H_2SO_4, HIO_3 (135-136).

4. Non-volatile and stable acids may be prepared by treating a solution of a salt of the desired acid with another acid giving a precipitate. H_3BO_3, H_4SiO_4, as well as many of the organic acids (85-86).

Bases. Alkalies. 1. By the solution of the metal in water. NaOH, KOH (637).

2. By the solution of the basic oxide in water. KOH, NaOH, $Ca(OH)_2$, $Ba(OH)_2$, $Mg(OH)_2$ (669, 691, 706).

FIG. 28

3. By treating an alkali carbonate with calcium hydroxide. NaOH, KOH (637).

4. By electrolysis of a salt. NaOH, KOH (640).

Insoluble bases. These are made by precipitating them from solution by the addition of a soluble base, such as sodium or potassium hydroxide (86).

Basic oxides. 1. By heating the metal in an atmosphere of oxygen. The metal is placed in a tube in the combustion furnace and heated to a red heat in a stream of oxygen (Fig. 27). CuO, Fe_2O_3, NiO, CoO.
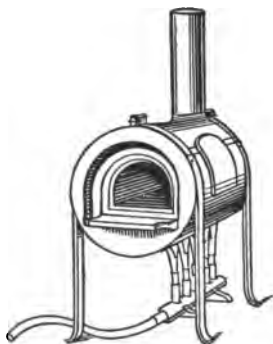
2. By heating the carbonate in the muffle-furnace (Fig. 28).

The oxides of almost all of the metals, except those of the first group, may be prepared in this way.

3. By heating the nitrate of the metal in the muffle-furnace. This method applies to nearly all of the metals except those of the first group.

4. By heating the hydroxide. Applies to nearly all metals except those of the first group.

Acid salts. These can be prepared from polybasic acids. Treat the metal, basic oxide, base, or normal salt with the proper excess of the acid or acid anhydride.

Normal salts. Some one of the following general methods will be found to be best adapted for the preparation of any given salt.

1. By treating a metal with an acid.

2. By treating a basic oxide with an acid.

3. By treating a base with an acid.

4. By treating an acid with the salt of a more volatile acid.

5. By double decomposition with the formation of an insoluble compound.

6. By melting together a basic with an acidic oxide.

7. By treating an alkali with an acid anhydride.

Preliminary considerations. Before undertaking the preparation of any chemical compound it is necessary to look up the properties of all of the substances concerned, especially their solubilities and specific gravities. If it is required that the compound should be chemically pure, it is desirable to make use of chemically pure materials.

Insoluble salts. Suppose it is desired to make a compound that is virtually insoluble in water. It is commonly made by mixing two solutions, one of which contains the basic radical and the other the acid radical of the required substance.

Select two chemically pure and soluble compounds and calculate exactly how many grams of each will be necessary to form the desired amount of the insoluble compound, being sure to take into account any water of crystallization that they may contain.

Look up their solubilities in water and dissolve each in hot

water and add enough cold water to make a cold saturated solution.

Filter the solutions and add one solution to the other very slowly with violent stirring.

Test a small portion on a suction filter to see if it can be filtered and washed.   If it is found possible to filter it in this way, wash it rapidly by decantation, pouring the washings through a large suction filter, finally transfer all the material to the filter, and wash by pouring water through it until the washings show no test for the acid radical of the other compound formed.

If it is impossible to filter and wash it on the filter, let it settle in a narrow, deep vessel overnight and siphon off the wash water the next day.   Add more water, stir thoroughly, let settle, and siphon again.   Repeat this as many times as necessary to get rid of the other compound present; or it might be filtered through an ordinary folded filter.

Soluble salts.   Look up the solubility of the salt at 100° C. and at 20° C.   The difference between these will be approximately the amount of the salt that will crystallize out of 100 c.c. of a hot saturated solution when it cools down to 20° C. If it is desired to have 100 g. crystallize out, as many hundred cubic centimeters of a hot saturated solution will be necessary as this difference is contained in 100.

Having found the volume of the saturated solution, find how many grams of the substance will have to be made to saturate it.   From this compute the quantities of the materials necessary.

The final solution is filtered hot, and the hot filtrate, in a beaker or flask well covered, is thoroughly wrapped up in cloth to cause it to cool very slowly, thereby forming large crystals, and left to stand overnight.

If pure materials have been used the product is essentially chemically pure.   In any case it may be recrystallized several times if necessary to render it more pure.

To find the number of cubic centimeters of acid to use, the theoretical weight of the acid is divided by the quantity of acid in 1 c.c. of the solution.   If much dilute acid is to be used, it will be necessary to take the water it contains into account in

computing the quantity of water to add to make up the required volume.

Example. Suppose it is desired to make potassium sulphate and have 200 g. crystallize out from solution. From an inspection of the table of solubilities (page 240), it appears that 100 c.c. of water at 100° C. dissolve 26 g. of this salt, and at 20° C. 11 g. Therefore, on cooling 100 c.c. of such a solution from 100° to 20°, 15 g. of the salt would crystallize out. In order to have 200 g. crystallize, it would be necessary to have as many hundred cubic centimeters as $\dfrac{200}{15}$, which equals 13.33, or 1333 c.c. Such a volume of solution saturated at 100° would contain 346 g. of K_2SO_4. It is now necessary to calculate the exact amount of acid and base necessary.

$$\begin{array}{ccc} 222 \text{ g.} & 195 \text{ g.} & 346 \text{ g.} \\ 2\,KOH\ + & H_2SO_4\ = & K_2SO_4\ + 2\,H_2O. \\ 112 & 98 & 174 \end{array}$$
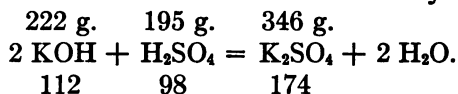
The quantity of KOH would be $\dfrac{112}{174} \times 346 = 222$ g., and the quantity of acid $\dfrac{98}{174} \times 346 = 195$ g. The KOH, being in the solid form, may be weighed out at once. It is necessary, however, to calculate the number of cubic centimeters of the acid. The specific gravity of the concentrated acid is 1.84, and it contains 98 per cent acid; 1 c.c., therefore, contains $1.84 \times .98 = 1.8$ g. As many cubic centimeters of the concentrated acid will be necessary as $\dfrac{195}{1.8} = 108.3$ g. 1300 c.c. of water are measured out into a 2-liter flask. The KOH is dissolved in a small portion of the water and the sulphuric acid diluted with another portion. The two solutions are carefully mixed in the flask, care being taken that the final solution is either exactly neutral or very slightly acid. The mixture should be kept boiling hot. On cooling, the excess of salt will crystallize out.

Questions on Exercise No. 38. State five general methods for the preparation of acids. State seven general methods for the preparation

of salts.　State five methods for the preparation of bases.　What is the common method for making sodium hydroxide?　State four general methods for the preparation of metallic oxides.　How may acid salts be prepared?　How are insoluble salts prepared?　How are the insoluble hydroxides prepared?

LABORATORY EXERCISES IN APPLIED CHEMISTRY

The following exercises are inserted for the benefit of pupils who do not intend to go to college, and may well be substituted for some of the preceding exercises relating exclusively to the study of the metals.

LABORATORY EXERCISE No. 39

Determination of the Percentage of Insoluble Residue and Examination of the Filtrate

Materials.　Wood-ash; alcohol; barium chloride solution; molybdate solution; potassium ferrocyanide solution.

Apparatus.　Funnel-tube; lamp-stand; mortar; balance; beaker; platinum wire.

· 1. Weigh accurately a disk of filter-paper and fit it to the funnel-tube, moistening it to make it stay.　Pass the funnel-tube through the clamp of the lamp-stand.　Place about 3 g. of wood-ash in the mortar and grind any lumps to a powder. Weigh out accurately exactly 2 g. of this powder on a counterpoised watch-glass.　Transfer the weighed wood-ash to the beaker and add 10 c.c. dil. HCl.　What does the effervescence indicate?　Heat to boiling and boil down to one-half the bulk.　Add ½ t.t. of boiling water and filter, allowing the filtrate to run into a bottle.　Rinse the beaker repeatedly with hot water and see that all of the undissolved portions are transferred to the filter.　Remove the bottle containing the filtrate; replace it with another bottle.　Wash the filter-paper by pouring hot water over it until the water running through no longer reddens blue litmus paper.　Remove the filter-paper with its contents.　Press it between sheets of filter-paper to remove most of the moisture, and either dry it in the drying-oven or let it·

stand until the next laboratory exercise. When it is dry re-
weigh it. Subtract the weight of filter-paper. The difference
is the undissolved residue. Divide this by the weight of the
original substance taken, and multiply by 100. The result is
the percentage of residue.

2. **Sodium and potassium.** While the filter is drying boil
1 g. of wood-ash in test-tube with 10 c.c. of water and filter into
another test-tube. Test the filtrate with litmus paper. Make
a loop on the end of a platinum wire. Dip it into the liquid
and introduce the wet end into the flame. Examine the flame
through the blue glass. Do you find evidence of sodium or
potassium? (Page 85.)

3. **Sulphate.** To a portion of the HCl solution diluted with
water add a little BaCl₂ solution. A white precipitate indi-
cates the presence of the sulphate radical.

4. **Phosphates.** Add to another portion of the acid filtrate
some ammonium molybdate solution, and heat not quite to
boiling. A yellow precipitate indicates the presence of phos-
phates.

5. **Iron and aluminum.** Add an excess of ammonium hy-
droxide solution to another portion of the filtrate and heat to
boiling. Let settle. The gelatinous precipitate consists of
a mixture of the hydroxides and phosphates of iron and alu-
minum. To another portion add potassium ferrocyanide solu-
tion. The blue precipitate shows iron.

6. Determine the percentage of water or acid insoluble in
samples of other substances, such as sapolio, earth, tooth-pow-
der, baking-powder, etc.

Questions on Exercise No. 39. State the exact procedure necessary
to determine the percentage of water or acid-insoluble residue in a sample.
Why is it necessary to wash the filter-paper after the filtration? How
should you test a substance for a carbonate; a sulphate; a phosphate; iron?
How should you have determined directly the percentage of soluble mat-
ter? What is a test for sodium? potassium?

LABORATORY EXERCISE No. 40

Extraction

Materials.   Tea; ferrous sulphate; vanilla-beans; alcohol; sugar; lead acetate.

Apparatus.   Funnel.

Definitions.   Decoction.   An extract made by soaking or boiling a substance in water.

1. **Examination of tea.**   Commercial tea is likely to be adulterated by the addition of spent tea-leaves.   Determine the percentage of soluble matter in a sample of tea as follows: place 2 g. of tea leaves in a funnel fitted with a weighed filter-paper.   Pour boiling water through it until the filtrate runs through colorless.   Take out the paper with its contents, fold it together, and allow it to dry until the next laboratory exercise.   When dry weigh it.   Subtract the weight of the filter-paper.   The difference will be the weight of the extracted leaves.   The difference between this and the original weight of the sample taken is the weight of matter extracted.   Divide this loss in weight by 2 and multiply by 100.   The result is the percentage of soluble matter.

2. **Tannin in tea.**   Place about 1 g. of tea in each of two test-tubes.   Fill each tube half full of boiling water.   Allow one to stand for five minutes and gently boil the other for the same time.   Test for tannin by adding some of each kind of tea to test-tube containing equal amounts of ferrous sulphate solution.   A dark-blue color indicates the presence of tannin. Dilute each tube with water and decide which process of making tea extracted the greatest amount of tannin.   Tannin extracted from the bark of trees is used in converting hides to leather.   Is it desirable to have a great quantity of tannin in the tea?

3. Test decoctions of other vegetable matter for tannin, especially nutgalls, oak leaves, potato skins, hemlock bark, coffee.   Ink is sometimes made by adding ferrous sulphate to a decoction of nutgalls together with some gum arabic.

4. **Extraction of thein.**   Both tea and coffee contain an alka-

loid called **thein.** The thein may be extracted from tea as follows: boil a teaspoonful of tea with about 50 c.c. of water. Filter the decoction. Cool the filtrate in a flask by letting water run over the outside. Transfer the liquid to a separatory funnel (Fig. 29) and add about one-fifth its bulk of chloroform. Insert the stopper and shake thoroughly. Let it stand until the two liquids have separated. Remove the stopper and allow all of the chloroform to run out into a watch-glass. Much of the thein is contained in the chloroform. After the evaporation of the solvent the alkaloid will be left on the glass.

Fig. 29

5. **Extract of vanilla.** Extract of vanilla is made by extracting the oil from vanilla-beans with alcohol and sweetening the product with a little sugar. Place in a small bottle 4 g. of ground vanilla-beans, add 4 g. of sugar, 20 c.c. of alcohol, and 10 c.c. of water. Cork the bottle and allow to stand for a week or more. Then filter. The filtrate is a fair extract of vanilla. It should give a brown precipitate with 10 per cent lead acetate solution, which will distinguish true vanilla from artificial. Bring a small sample of vanilla extract from home and test it to see whether it is natural or artificial.

Questions on Exercise No. 40. Define the term "decoction." How should you determine the percentage of soluble matter in tea? Which contains the more tannin, tea that is made by steeping the leaves in water or that made by boiling them in water? What is the test for the presence of tannin? What is extract of vanilla? How should it be made? How could you distinguish between pure and artificial vanilla?

LABORATORY EXERCISE No. 41

Fermentation and Distillation

Materials. Molasses; yeast; lime-water; acetic acid.
Apparatus. Liebig condenser; 500-c.c. flask; lamp-stand.

1. Dissolve ½ t.t. full of molasses in 150 c.c. of water heated until it is lukewarm. Dissolve ½ yeast-cake in 150 c.c. of water, also just warm to the hand. Mix these two solutions in a 500-c.c. bottle. Fit the bottle with a stopper and delivery-tube. If a two-hole stopper is used, plug one of the holes

Allow the delivery-tube to dip into a test-tube filled with lime-water. Wrap the bottle in a towel and put it away for three or four days. Note from time to time what is going on in the test-tube. The molasses is changed to alcohol, and carbon dioxide is given off.

2. At the next exercise arrange a Liebig condenser and flask as shown in Fig. 30. Place 200 c.c. of the fermented liquid in
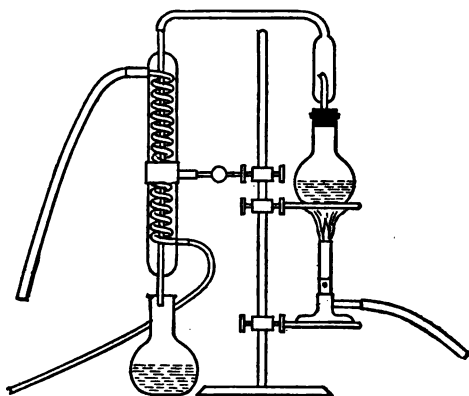
Fig. 30

the flask and distil off 100 c.c. Wash out the flask and pour the distillate back into it. Distil off 10 c.c. Smell the distillate. See if a drop of the liquid on the end of a splint will burn. What is it? To a small quantity of this alcohol in a test-tube add an equal bulk of acetic acid and a few drops of concentrated sulphuric acid. Heat the mixture and note the odor of ethyl acetate.

3. Distil other liquids suspected of containing alcohol, such as patent medicines, cider, wine, tinctures, and extracts, and see if it is possible for you to prove that alcohol is present.

4. **Determination of the per cent of alcohol.** Measure exactly 100 c.c. of the liquid to be tested into the distilling flask and distil off about one half. Add distilled water to the distillate until the volume of the mixture is exactly 100 c.c. Determine the specific gravity of the mixture in any suitable manner, and find the percentage of alcohol from a set of tables. The weight of 1 c.c. in grams is the specific gravity.

<center>LABORATORY EXERCISE No. 42</center>

Ethereal Salts. Compound Ethers, or Esters. Saponification

Materials. Alcohol; sodium acetate; vegetable oil.

Apparatus. 300-c.c. side-neck distilling bulb; Liebig condenser; lamp-stand.

Definitions. Alcohols. Methyl alcohol (wood alcohol), CH_3OH; ethyl alcohol (common alcohol), C_2H_5OH; propyl alcohol, C_3H_7OH; amyl alcohol, $C_5H_{11}OH$; glycerine, $C_3H_5(OH)_3$.

Ethereal salts. When an alcohol is treated with an acid in the proper manner, the acid radical of the acid replaces the hydroxide of the alcohol and forms an ethereal salt. The action is something like the action of an acid on a base.

$$NaOH + HNO_3 = NaNO_3 + HOH.$$
$$CH_3OH + HNO_3 = CH_3NO_3 + HOH.$$
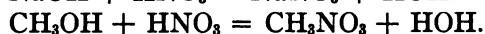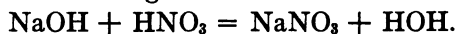
The compound CH_3NO_3 is known as methyl nitrate. Other alcohols would react with acids in a similar way.

1. **Preparation of ethyl acetate,** $C_2H_5C_2H_3O_2$. Arrange a 300-c.c. side-neck distilling bulb with a Liebig's condenser, as shown in Fig. 31. Place in the bulb 60 c.c. conc. sulphuric acid (run
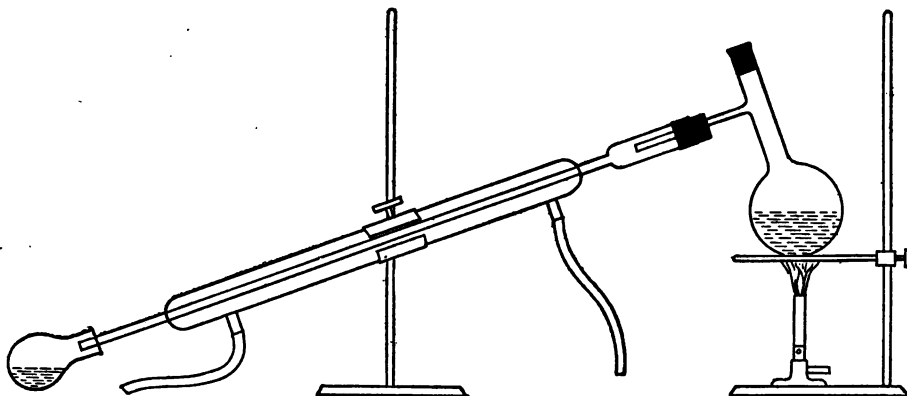
FIG. 31

it in through the funnel-tube), 40 c.c. of alcohol, and 60 g. of sodium acetate. Put a cork stopper in the distilling bulb, and heat cautiously over the wire gauze. Have a slow stream of water flowing through the condenser. Collect about 50 c.c. of the distillate. Note its fruity odor. Allow the liquid in the bulb to cool as long as possible, then pour it into the beaker and let it stand until cold. Flush the sink with a great quantity of water when the acid solution is finally thrown away.

2. **Saponification.** If a metallic salt be treated with an alkali,

it is ordinarily changed to the hydroxide of the metal and another salt:

$$FeCl_3 + 3\,NaOH = Fe(OH)_3 + 3\,NaCl.$$
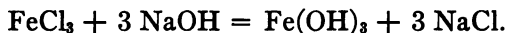
If an ethereal salt be treated with an alkali a similar reaction takes place, but not so readily:

$$C_2H_5C_2H_3O_2 + NaOH = C_2H_5OH(alcohol) + NaC_2H_3O_2.$$

This process is called saponification, for the reason that the making of soap from grease by the action of an alkali is a similar reaction.

3. **Fats and oils** are ethereal salts of the triacid alcohol glycerine, with various organic acids. Beef tallow is glycerine tri-stearate, $C_3H_5(C_{17}H_{35}CO_2)_3$. Vegetable and animal oils contain glycerine tri-oleate, $C_3H_5(C_{17}H_{33}CO_2)_3$. If a fat be boiled with an alkali, it is **saponified** with the formation of a salt of the fatty acid and glycerine. The salt of the fatty acid is soap:

$$C_3H_5(C_{17}H_{35}CO_2)_3 + 3\,NaOH = 3\,NaC_{17}H_{35}CO_2 + C_3H_5(OH)_3.$$
$$\quad\text{stearine}\qquad\qquad\qquad\text{soap}\qquad\quad\text{glycerine}$$
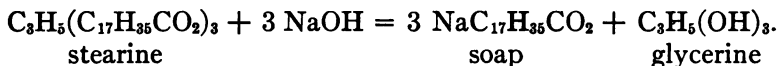
4. Place 5 c.c. of a vegetable oil in a bulb test-tube with 10 c.c. of a 20 per cent solution of sodium hydroxide. Boil gently for ten minutes, adding water from time to time to make up any loss by evaporation. When the reaction is complete, as shown by the uniform nature of the contents of the tube, add 2 g. of salt and allow the tube to stand until the next exercise. The solid material which rises to the top of the liquid is soap.

5. Dissolve some good soap, cut into small pieces, in boiling water in the beaker. Add some of this to a bottle of water containing about a gram of calcium chloride. A precipitate of insoluble calcium soap is formed. This is the kind of reaction which soap brings about in hard water. The water will not be softened until all of the calcium or magnesium has been converted into the corresponding insoluble soap.

Questions on Exercise No. 42. Name four different alcohols. What is an ethereal salt? Write reactions between four different alcohols and several different acids. Name the ethereal salts. How did you make ethyl acetate? What would take place if an ethereal salt were boiled with an alkali? What is meant by saponification? What is the chemical nature of fats and oils? What is the effect of boiling a fat or oil with

an alkali? What is soap? What would be the effect of treating a soap with a mineral acid? What is meant by hard water? What is the scum which forms when soap is used with hard water? (678).

LABORATORY EXERCISE NO. 43

Hard Waters and the Purification of Water (678; 338)

Materials. Broken marble; lime-water.

Apparatus. Bottle; lamp-stand; funnel-tube; Liebig condenser; 500-c.c. flask.

Definitions. Hard water. Water containing salts in solution, the metals of which form insoluble soaps.

    Water of temporary hardness. Water containing bicarbonates of metals in solution which are precipitated by boiling.

    Water of permanent hardness. Water containing salts in solution which are not precipitated by boiling and which form insoluble soaps.

1. **Water of temporary hardness.** Place 100 c.c. of lime-water in a bottle. Set up a carbon dioxide generator and pass CO_2 through the lime-water until the precipitate formed at first is entirely redissolved. The calcium carbonate unites with the excess of carbonic acid to form acid calcium carbonate, $H_2Ca(CO_3)_2$, which is soluble.

2. Divide the clear solution into two parts. Place one part in the beaker and boil it. Shake the other with a piece of soap and note the precipitate of calcium soap that is formed. Other metals besides calcium might be present in natural waters in the form of bicarbonate, especially iron and magnesium.

3. **Water of permanent hardness.** Place about 100 c.c. of distilled water in a bottle. Shake it with a piece of soap and note that suds form at once. Repeat with distilled water to which about a gram of calcium chloride has been added. No suds will form until all of the calcium has been precipitated as insoluble soap. Make another solution of calcium chloride in distilled water as before, but before shaking with soap add as much dry sodium carbonate as you did calcium chloride. A precipitate of calcium carbonate is formed. The water should not form suds at once.

4. Purification by distillation. Set up a Liebig's condenser and distilling bulb, as shown in Fig. 31. Place in the flask a solution of water containing calcium chloride, a drop or two of sulphuric acid, and some potassium permanganate solution. Distil over some pure water. How could you prove that it contains no chloride, sulphate, or acid?

Questions on Exercise No. 43. What is hard water; water of temporary hardness; water of permanent hardness? What would be the effect of adding an alkali to water of temporary hardness? · What happens when such water is boiled? How may water of permanent hardness be softened? What metals are usually found in hard water? How did you prepare water of temporary hardness? What effect has soap on hard water? What is the formula of calcium stearate? Which substance would be the cheaper to use in the softening of water, soap or sodium carbonate? What is the objection to using a hard water in a boiler? How might such a water be treated to render it fit for use?

LABORATORY EXERCISE No. 44

Examination of Cloth

Materials. Cotton cloth; woollen cloth; ether; alcohol.
Apparatus. Test-tubes; beaker; lamp-stand.

1. Weigh out about 1 g. of cotton cloth. Boil it in beaker or test-tube in 20 per cent sodium hydroxide solution for about three minutes. Decant the liquid, rinse with water several times. Replace in beaker, cover with water, add 1 or 2 drops of phenol-phthalein and .enough dil. HCl to decolorize. Rinse several times, dry on wire gauze well above the flame. Weigh. Has any dissolved?

2. Boil some woollen cloth or yarn in sodium hydroxide just as you did the cotton. If you boiled a piece of cloth containing both cotton and wool, which substance would dissolve? How could you estimate the percentage of wool in a piece of cloth?

3. Weigh out about 2 g. of a piece of cloth known to contain both cotton and wool. Boil it for three minutes in 20 per cent sodium hydroxide solution. Wash the residue as above, dry, and weigh. Divide the loss in weight by the weight of cloth taken, and multiply the result by 100. The result is the per cent of wool in the cloth.

4. Determine the percentage of wool in several pieces of cloth of different kinds.

5. Examine both cotton and wool fibres under the microscope. Make drawings bringing out the chief points of difference between the two.

6. Burn a little cotton and note the odor. Burn some wool.

Questions on Exercise No. 44. How could you determine the percentage of wool in a piece of cloth? In what does wool dissolve? In what other way could you detect the presence of both cotton and wool? Describe the appearance of cotton fibre under the microscope; the appearance of wool.

LABORATORY EXERCISE No. 45

Lakes and Dyeing

Materials. Logwood; alum; cochineal; nun's-veiling; colored gelatine; aluminum acetate.

Apparatus. Beaker; lamp-stand.

Definitions. Decoction, a water extract.

Lake. A colored substance formed by precipitating an aluminum or tin salt in a solution colored with an organic coloring matter.

Mordant. A substance into a solution of which the cloth is dipped previously to dyeing, in order to cause the color to adhere to the fibres.

1. **Lakes.** Make a decoction of logwood by boiling about 10 g. of logwood chips in 100 c.c. of water in the beaker for five minutes. Decant or filter the solution. Add about 2 g. of powdered alum. Stir to dissolve. Make alkaline with ammonium hydroxide. Let settle. The precipitate of aluminum hydroxide carries down the color with it and constitutes a lake. If this were filtered off, dried, and ground, it would form a colored pigment.

2. Repeat with a solution of cochineal, also with turmeric.

3. Dip a piece of cloth in a solution of aluminum acetate and dry it. Place this cloth together with another piece that has not been treated with a mordant in a solution of logwood

or cochineal and boil for five or ten minutes. Remove the two pieces of cloth and note which has taken the dye.

4. Repeat the dyeing with the other available colors.

5. **Detection of aniline dyes.** Many substances used as food are colored with coal-tar dyes. Examples of some of these are: gelatine, catchup, wines, sirups, jellies, jams, candy. The simplest method of detecting these dyes is the double-dyeing process of Sostegni and Carpentieri. It consists in boiling a piece of woollen cloth in an acidified solution of the colored substance. The color is then dissolved from the cloth by boiling in a weak ammonia solution. This extracted color is then acidified with HCl and a fresh piece of cloth is boiled in it.

6. Boil 20 g. of the substance to be tested with 100 c.c. of water until the solution is strongly colored. Filter if necessary. Prepare a piece of woollen cloth, 4 in. square, preferably nun's-veiling, by boiling in a 1 per cent solution of sodium hydroxide and then in water. Wash it thoroughly and dry by pressing between filter-paper. Add 2 c.c. of dil. HCl to the colored liquid and boil the cloth until it is strongly colored, five or ten minutes. Remove the cloth, rinse it thoroughly, and boil in 100 c.c. of water to which 5 c.c. of dil. HCl has been added. Remove the cloth from this solution and wash it thoroughly. Dissolve the color from the cloth by boiling it in 50 c.c. distilled water to which 1 c.c. of concentrated ammonia or its equivalent has been added. Discard the old piece of cloth. Make the ammoniacal solution slightly acid with HCl and boil a fresh piece of cloth very much smaller than the first. In the case of aniline dyes this second piece of cloth will become highly colored. While natural vegetable colors might have dyed the first piece they will not impart much of any color to the second piece.

7. Bring various substances from home and test them as above for artificial coloring matters.

Questions on Exercise No. 45. What is a lake? What is a mordant? What are two common mordants? What happens when aluminum hydroxide is precipitated in a solution containing a vegetable coloring matter? How may aniline dyes be detected in food materials?

LABORATORY EXERCISE No. 46

Examination and Preparation of Tooth-Powders

Materials. Samples of tooth-powder; molybdate solution.
Apparatus. Test-tubes.

Tooth-powders generally consist of finely divided cal-
cium carbonate, known to the druggists as "precipitated
chalk," mixed with other substances. They may contain
powdered pumice-stone or cuttlefish-bone. Both of these
are undesirable, as they scratch the enamel of the teeth.
The powder is usually sweetened and flavored.

1. **Sugar.** Boil about a gram of the powder with water in
test-tube and filter. Evaporate the filtrate in the porcelain
evaporating-dish to dryness. If sugar is present it will be
recognized by the odor when burned.

2. **Pumice-stone.** Dissolve about a gram of the powder in
5 c.c. of dilute nitric acid. Any insoluble residue would indi-
cate pumice. If present, dilute with 10 c.c. of water and filter
into test-tube.

3. **Phosphoric acid.** If this is present it probably came from
the cuttlefish-bone. Add an equal bulk of ammonium molyb-
date solution to the nitric acid filtrate from the last. Shake
the test-tube thoroughly and heat nearly to boiling. A yellow
precipitate indicates the presence of the phosphate radical.

4. **Calcium.** Dissolve some of the powder in the smallest
quantity of HCl. Moisten the end of a clean iron wire with
this solution and introduce it into the flame. A red color
shows calcium. Filter or decant some of the HCl solution into
a test-tube and add a little sulphuric acid. There should be a
precipitate of calcium sulphate.

5. **Preparation of tooth-powder.** Mix in a large mortar 50 g.
of precipitated chalk, 10 g. of powdered sugar, 5 g. of sodium
per-borate. Grind until thoroughly uniform. Dissolve 5 c.c.
of artificial oil of wintergreen in 20 c.c. of ether. Sprinkle
this solution well over the powder in the mortar. Grind the
whole together until all of the ether has evaporated and the

whole is a perfectly dry powder.   Place the product in a bottle, take it home, and use it.

Questions on Exercise No. 46.   What is the common ingredient of tooth-powder?   What harmful ingredients may tooth-powder contain?   How may pumice-stone be detected; cuttlefish-bone?   How could you make a serviceable tooth-powder?

LABORATORY EXERCISE NO. 47

Examination of Baking-Powders (530–534)

Materials.   Samples of all kinds of baking-powders; ammonium molybdate solution; iodine water; barium chloride solution; silver nitrate; lime-water; ammonium oxalate solution.

Apparatus.   Test-tubes; mortar; porcelain crucible; triangle; lamp-stand.

Baking-powders.   Baking-powders consist of sodium bicarbonate mixed with an organic acid, an acid salt, or a salt that reacts acid.   They may contain tartaric acid, or cream of tartar, acid phosphate, or alum.   When moistened with water carbon dioxide is set free by the action of the acid on the bicarbonate.   Starch is sometimes added to make them keep.

1. **Carbon dioxide.**   Moisten the sample with water and prove that the gas given off is CO_2.

2. **Starch.**   Boil a small quantity with water and add a drop of iodine water.   A blue color indicates starch.

3. **Sulphate.**   Shake a portion with water and filter.   Add barium chloride to the filtrate.   A white precipitate insoluble in HCl indicates the presence of sulphates, which probably means the presence of alum.

4. **Tartrates.**   Place about 5 c.c. of silver nitrate in a test-tube.   Add ammonia until the precipitate which forms at first is just redissolved.   Then add some of the above filtrate from the powder.   Boil.   If tartrates are present a beautiful deposit of silver will form on the inside of the tube.

5. **Phosphates.**   Add some of the water extract to 10 c.c. of

ammonium molybdate solution in a test-tube and heat. A yellow precipitate indicates the presence of phosphates.

6. **Ammonia.** Moisten some of the powder in a mortar with sodium hydroxide, grind with the pestle, and smell for ammonia.

7. **Aluminum.** Burn about 2 g. of the sample in a small porcelain crucible to a white ash. When the crucible is cold boil some water in it to extract the soluble portion. Filter and add ammonium chloride to the filtrate until it smells of ammonia. A white gelatinous precipitate indicates aluminum.

Questions on Exercise No. 47. What is the general nature of a baking-powder? What are three general classes of baking-powders? Name three substances that would liberate CO_2 from bicarbonate of soda in the moist condition. Describe tests for starch; carbon dioxide; sulphate; tartrates; phosphate; ammonia; and aluminum.

PART II

FUNDAMENTAL IDEAS

CHAPTER I

INTRODUCTION

1. **Chemistry and physics.** In both physics and chemistry we have to do with the study of matter in its relation to space, time, and energy. In physics we have to do with definite quantities of matter as a whole in its relation to space, time, and energy. A lead bullet fired from a gun goes a certain distance in a certain time and possesses a definite quantity of dynamic energy. In chemistry we have to deal with the changes that take place within the matter itself and not on the original unaltered substance. The same lead bullet may be operated upon in such a way that it will lose all the appearance of lead and be converted into a yellow powder. Such changes also involve space, time, and energy, for the powder occupies more space than the original lead. It required energy to bring about the change, and the change required an appreciable time.

2. **Importance of a knowledge of matter.** Matter may be defined as that which has weight. Every operation with which we are familiar, from the simplest one of our daily home life to the most complicated one of the manufacturing industries, has to do with matter in some form—solid, liquid, or gaseous. It is inconceivable that there could be an occupation or industry of man that does not depend for its success on a knowledge of the peculiarities of the particular kinds of matter concerned. It follows, then, that a study of matter in its various forms and changes would lead not only to the more intelligent conduct of our daily lives but to the more successful prosecution of whatever occupation we happen to be engaged in.

3. **Elements.** An element is a substance that contains but one kind of matter. It is impossible, by any known operation, to extract from an element any kind of matter different from the element itself (696). Examples of simple substances known as elements are gold, silver, copper, tin, lead, iron, and oxygen. About eighty such elements have been discovered, of which only about twenty-six are common.

4. **Symbol of an element.** The symbol of an element is a sign that stands for that substance. It generally consists of one or two characteristic letters of the English or Latin name.

Symbols and names of some elements in groups.

GROUP 1		GROUP 2		GROUP 3		GROUP 4	
H,	Hydrogen.	Mg,	Magnesium.	B,	Boron.	C,	Carbon.
Na,	Sodium.	Ca,	Calcium.	Al,	Aluminum.	Si,	Silicon.
K,	Potassium.	Zn,	Zinc.			Sn,	Tin.
NH₄,*	Ammonium.	Ba,	Barium.			Pb,	Lead.
Ag,	Silver.	Hg,	Mercury.				

GROUP 5		GROUP 6		GROUP 7		GROUP 8	
N,	Nitrogen.	O,	Oxygen.	F,	Fluorine.	Fe,	Iron.
P,	Phosphorus.	S,	Sulphur.	Cl,	Chlorine.	Ni,	Nickel.
As,	Arsenic.	Cr,	Chromium.	Br,	Bromine.	Co,	Cobalt.
Sb,	Antimony.			I,	Iodine.		
Bi,	Bismuth.						

5. **Chemical composition.** The chemical composition of a substance means the relative proportions by weight of all the elements contained in it. This is most easily expressed in per cents. Thus, marble contains 40% calcium, 12% carbon, and 48% oxygen. The process of ascertaining the chemical composition of a substance is called **analysis.** When only the kinds of elements contained in the substance are desired, the process used is called **qualitative analysis;** and when the exact proportions by weight are desired, it is called **quantitative analysis.**

6. **Physical change.** A physical change is one in which the chemical composition of the body is not altered. A body may be set in motion, heated, magnetized, electrified, pulverized, melted, gasified, or dissolved, generally without changing its chemical composition.

* Not an element but a compound of N and H which acts like one.

7. Chemical change. A chemical change is usually one in which the chemical composition of the body is altered. Such changes are always accompanied by some change in the total energy which is associated with the substances concerned. That is, there is an evolution or absorption of heat, light, or electricity. If sugar be heated hot enough, it changes into carbon and water. In this case there must have been an absorption of heat. If carbon be heated in oxygen, it changes into a colorless gas called carbon dioxide. In this case there was an evolution of both heat and light. If two different metals be connected in the same solution, there is an evolution of electricity, and one or both of the metals undergo a chemical change.

8. Properties of matter. Properties of matter are those qualities which are peculiar to or characteristic of it. A complete description of any kind of matter involves telling what it looks like, how its tastes and smells, how it behaves when heated or cooled, and especially what happens when it is mixed with other substances.

Most of the elements and many complex substances can exist in three states—as a solid, a liquid, or a gas. Heating without pressure tends to change solids and liquids to the liquid or gaseous form. Cooling gases under pressure causes them to become liquid. Some gases may be liquefied at the ordinary temperature by either pressure or cold.

Properties of matter may be divided into three kinds: **physiological, physical,** and **chemical.** By physiological properties we mean how the matter affects the human system either internally or externally. By physical properties we mean its appearance and state, how it is affected by pressure and heat or cold, degree of solubility in various liquids in which it undergoes no chemical change, how its volume changes with a change of pressure, and the weight of a unit volume. By chemical properties we mean chemical changes that it can take part in, with the circumstances or conditions under which they take place. This constitutes the chief part of the study of chemistry.

9. Atoms and molecules. All matter is supposed to be made up of a very large number of very small particles called mole-

cules, and these molecules to be made up of still smaller particles called atoms.

10. Molecule. A molecule is the smallest particle of matter that can exist and still retain most of the properties of that kind of matter.

If the substance is an element, the molecule will consist of one or more atoms of that element; if the substance is a chemical compound, the molecule will contain at least one atom of every element contained in the substance.

11. Atom. An atom is the smallest particle of an element that forms part of a molecule.

12. Chemical compound. A chemical compound is one containing the elements mixed in such a way that they cannot be separated by mechanical means. It always has exactly the same chemical composition, and all of the smallest visible particles look alike under the microscope.

A chemical compound contains only one kind of molecule. If sulphur and iron be heated together, a compound called iron sulphide is formed; and no mechanical process can separate them. Each molecule of the substance contains one atom of iron and one atom of sulphur.

13. Mechanical mixture. A mechanical mixture is one containing elements or compounds mixed in such a way that they may be separated by mechanical means. The iron and sulphur could readily have been separated by a magnet before they had been heated. A mixture of sugar and sand could readily be separated by dissolving the sugar in water; and the sugar could then be obtained from the water by allowing the latter to evaporate.

Solutions resemble chemical compounds in that all parts of the same solution have exactly the same chemical composition, and it is impossible to distinguish different kinds of particles by means of the microscope.

However, the solvent can usually be evaporated in the pure condition, leaving the other substance by itself either in the liquid or solid form.

A mechanical mixture contains at least two different kinds of molecules.

14. Relative abundance of elements. Oxygen is by far the most abundant of all the elements, forming about one-half the whole weight of the earth. This is readily comprehended when it is understood that oxygen forms more than one-half the weight of ordinary sand, eight-ninths the weight of water,

OXYGEN 50%

SILICON 25%

ALUMINUM 8%

IRON 6%

CALCIUM 4%

MAGNESIUM 2%

POTASSIUM 2%

SODIUM 2%

ALL OTHER ELEMENTS 1%
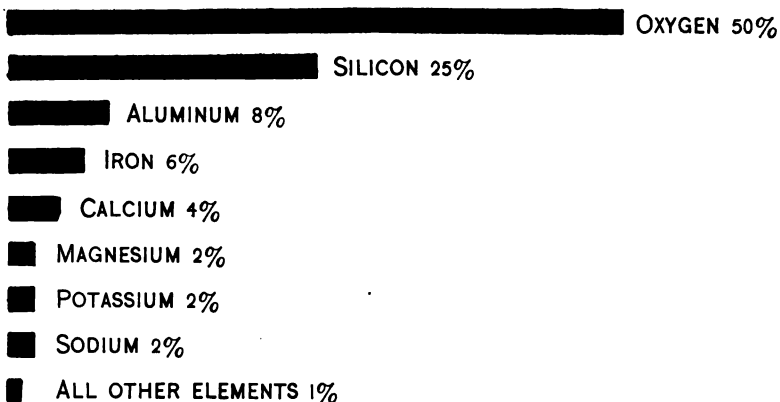
FIG. 32

about one-fifth the weight of air, and from 40% to 60% of the weight of most rocks. Silicon comes next, forming about one-fourth the weight of the earth. Sand is nearly one-half silicon, and many rocks contain about 25% of it. Aluminum forms about 8%, iron 6%, calcium 4%, and all the remaining elements 7% of the weight of the earth. This is graphically shown in Fig. 32.

15. Occurrence of the elements. Comparatively few of the elements occur in the free condition; that is, not combined with other elements. Those that are commonly said to be found in the free condition are usually mixed with other elements or compounds.

Oxygen occurs in the free condition in the air, but it is mixed with nitrogen and other gases. Gold is said to occur in the free condition; but it is not only alloyed with silver but is mixed with large quantities of sand and rock.

The majority of substances with which we come in daily

contact are mechanical mixtures of chemical compounds. In fact, it is a very difficult matter to obtain a perfectly pure element or compound. Even the pure chemicals bought in the market must be examined to see if they contain sufficient impurity to interfere with their use.

The substances studied in this book are in all cases supposed to be the strictly chemically pure material. The slightest trace of an impurity often endows the substance with very different properties from those of the pure material.

16. Value of the study of chemistry.

(*a*) It teaches us the properties and uses of forty or more elements or compounds that are involved in our daily life and are to be found in or about almost every house. Among them we have silver, gold, zinc, mercury, aluminum, carbon, tin, lead, nitrogen, phosphorus, oxygen, sulphur, iodine, iron, nickel, copper, and perhaps platinum. Among the compounds we have common salt, soda, lye, cream of tartar, blue vitriol, magnesia, lime, lime-water, whitewash, zinc white, calomel, corrosive sublimate, sand, red lead, white lead, chrome yellow, calcium phosphate (in fertilizers), white arsenic, ammonia, iron oxide, sugar, starch, alcohol, vinegar, and kerosene. There are many others that might easily be thought of. Surely, even an elementary knowledge of these things ought to lead to a more intelligent, happier, and perhaps longer life.

(*b*) It trains the student in exact habits of observation and of thought. It teaches him to be precise in the use of language and to write intelligent reports in good English on work done. These are accomplishments that are highly appreciated by the employer.

(*c*) As a disciplinary study it is quite equal to mathematics, language, or history.

17. Source of the facts of chemistry. All the facts of chemistry have been obtained by the direct observation of or experimentation with matter itself in its various forms or when in contact with other kinds of matter. The student seldom appreciates that if the printed facts relating to matter were traced to their original source it would be found that they originated with some investigator who learned them by close

and laborious observation and experiment. By observation we do not mean merely seeing, but feeling, hearing, tasting, and smelling as well.

Questions

THE BLACK-FACE NUMBERS REFER TO PARAGRAPHS

1. Distinguish between physics and chemistry (1). Define matter (2).
2. What is an element? (3). Five examples of common elements (3).
3. What is a symbol of an element? Give in fifteen seconds the symbols and names of all the common elements in groups (4).
4. Define the terms chemical composition, analysis, qualitative analysis, quantitative analysis (5).
5. Define the term physical change (6); chemical change. What always accompanies a chemical change? (7).
6. Give three examples of common chemical changes (7).
7. What is meant by properties of matter? In what three states may matter exist? Give three classes of properties of matter (8).
8. Of what is matter supposed to be made up? (9). What is a molecule? (10).
9. What is an atom? (11); a chemical compound? (12); mechanical mixture? (13).
10. Name five of the most abundant elements and state approximately what portion of the earth each forms (14).
11. Give three reasons for believing the study of chemistry to be desirable (16).

CHAPTER II

LAWS, THEORIES, AND HYPOTHESES

18. (*a*) **Laws.** When a sufficient number of observations relating to matter have been accumulated, it is possible to arrive at certain generalizations which cover a vast number of cases and not only help us to remember a large number of phenomena but enable us to predict the behavior of matter in a great many cases under various conditions. When such a generalization is found to hold true in every experimental test, it is called a **law.** Thus we have the **law of gravitation,** which states that any two particles of matter attract each other with a force which is proportional to the product of their masses and inversely proportional to the square of the distance between their centres of gravity.

Law of the conservation of matter. Matter can neither be created nor destroyed. In a closed system containing any quantity of matter undergoing any change or series of changes the total quantity of matter at the end is exactly the same as at the beginning.

Law of conservation of energy. Energy can neither be created nor destroyed. In a fixed quantity of matter undergoing any change the total quantity of energy involved is a constant.

(*b*) **Hypothesis.** When the observations and experiments still leave something to be desired in the way of detailed conditions necessary to account for the existence of the laws, then we make assumptions regarding the conditions which would account for them. Such an assumption is called **a hypothesis.**

(*c*) **Theory.** The whole mass of deductions relating to any one subject which are in any way dependent on hypotheses is called the **theory** of that subject. Thus we have the atomic and molecular theories, and the theory of light.

19. Matter and energy. It is quite impossible to think of energy without associating it with matter. We are very familiar with many of the kinds of energy that are ordinarily associated with matter. We have energy due to the position or motion of a piece of matter, to its tendency to expand or contract, to its condition of electrification or magnetization; and energy due to the heat that it actually possesses as a result of which it can raise the temperature of a body with which it comes in physical contact. Matter must also possess chemical energy. Carbon readily unites with oxygen and forms a chemical compound. During this action a large amount of energy in the form of heat is set free. Where did it come from?

Since energy cannot be created nor destroyed, we must assume that both the carbon and the oxygen contained a definite amount, that the carbon dioxide formed also contained a definite amount, but that the amount contained in the carbon dioxide was not equal to the sum of the two quantities of energy in the original elements, and therefore the difference must have been given out in the form of heat.

20. Kinds of chemical change. There are four kinds of chemical changes commonly met with in the laboratory: (1) Direct union of two or more substances with the formation of a single new compound, called **combination, or synthesis.** (2) Separation of a compound into two or more simpler substances, called **decomposition, or analysis.** (3) Sometimes parts of two different substances change places forming two new substances. Such changes are known as **double decompositions.** (4) One element may replace another in a compound. Zinc will replace hydrogen in an acid, setting the hydrogen free. Such changes are called **substitutions.**

21. Exothermal and endothermal reactions. Cause of chemical change. Every chemical change is accompanied by an evolution or absorption of energy in some form. Since this change must be an increase or decrease in the energy contained in the matter, we can divide all chemical changes into two classes: (1) Those in which there is a decrease in the energy contained in the substances, with an evolution of some form of energy.

As the lost energy usually escapes in the form of heat, such changes are called **exothermic.** (2) Changes in which energy is absorbed by the reacting substances. Changes of this class are called **endothermic.**

Equilibrium. Any system of chemical substances exists in a condition of equilibrium, either stable or unstable, with regard to the content of chemical energy. If it is an unstable condition, a comparatively small cause will upset the equilibrium and start a chemical change with the liberation of energy. This liberated energy aids in bringing about further change, and the reaction proceeds by itself to completion. The explosion of a train of gunpowder or the burning of any substance is a good example of this kind of change.

If the system of matter is stable with regard to its total chemical energy, it must be surrounded by conditions which will result in its gaining energy in order that a chemical change may be induced. In this case the energy is constantly absorbed as long as the change proceeds, and it is quite impossible for the reaction to propagate itself. Thus it is quite impossible that the nitrogen of the air should suddenly take fire and burn by combining with the oxygen of the air, for the reaction would be endothermic and could not propagate itself.

The common agencies for bringing about chemical changes are heat, light, electricity, and solution.

22. Catalysis. Many chemical reactions are either brought about or are very materially hastened by the presence of certain substances which are themselves left entirely unchanged at the end of the reaction. Such substances are known as **catalysers,** or **catalytic agents,** and the process is called **catalysis.** Water or water vapor is by far the most common catalytic agent. Many elements which ordinarily unite with great violence cannot be made to do so if they are absolutely free from water vapor. Very finely divided metals, especially platinum, as well as powdered non-metallic substances, act as catalytic agents. Manganese dioxide is used to hasten the evolution of oxygen from potassium chlorate in the laboratory preparation of the gas.

Questions

1. What is meant by a law? a hypothesis? a theory? (18).
2. State the law of conservation of matter; of conservation of energy (18).
3. What is a theory? (18).   Give examples of manifestations of energy accompanying chemical changes involving (*a*) heat, (*b*) light, (*c*) electricity, (*d*) force (19).
4. Mention four kinds of chemical change; what is an exothermic reaction? (21).
5. What is an endothermic reaction? (21).   Give examples of each kind.
6. Give an example of unstable equilibrium where, if a chemical change be started, it will go on to completion (21); one of stable equilibrium where the chemical change will not proceed by itself if once started (21).
7. What are the common agencies for starting chemical reactions? (21).
8. What is meant by catalysis?   Mention two catalytic agents (22).

CHAPTER III

ATOMIC AND MOLECULAR WEIGHTS, SYMBOLS, AND FORMULAS

23. Law of definite proportions. It has been ascertained by analysis of known chemical compounds that the elements combine with each other in definite proportions by weight. 35.5 weights of chlorine invariably combine with 23 weights of sodium, 39 of potassium, and 7 of lithium. Also that 16 weights of oxygen exactly combine with 24.36 weights of magnesium, 40 of calcium, and 65.4 of zinc. Other elements are equally fixed in their habits of combining. **In a given chemical compound the elements are always present in exactly the same definite proportions by weight.**

24. Law of multiple proportions. It has also been found that a given weight of a single element often forms several different compounds by combining with several different weights of a second element. Thus 7 weights of nitrogen combine with 4, 8, 12, and 16 weights of oxygen, forming four different oxides of nitrogen. **If a fixed quantity of one element unites with variable quantities of another, the weights of the variable element are simple multiples of the smallest.**

25. The atomic hypothesis of Dalton. As early as the fifth century B. C. certain philosophers considered all matter to be made up of small particles called "atoms." These atoms were all assumed to be of the same kind and the same size. Different kinds of matter were supposed to result from the atoms approaching or receding from each other.

In 1807 Dalton proposed the atomic theory which is in use to-day and is the basis of all modern theoretical chemistry. According to his theory, all the atoms of a given element are of the same size and the same weight, but atoms of different elements have different weights. If two or more atoms of the same kind unite, they constitute a molecule of an element. If

two or more atoms of different kinds unite, they form a mole-
cule of a compound.

This theory agrees with the **law of definite proportions** and the
law of multiple proportions, for, if two atoms unite to form a mole-
cule of a compound, the proportions of the elements in a mass
of the substance would be identical with the proportions by
weight of the elements in the molecule. Again, if a fixed weight
of one element unites with variable weights of another element
to form several different compounds, the ratios of the weights
of the variable element to each other are of the nature of simple
numbers.

This is well illustrated by the oxides of nitrogen. Twenty-eight
weights of nitrogen combine with 16, 32, 48, 64, and 80 weights
of oxygen. The ratio of the last four weights to the first is in
every case a simple whole number.

26. Atomic weights. The above facts, taken in connection
with others which cannot be considered here, have enabled
chemists to determine the relative weights of the various atoms.
It theoretically makes no difference in what terms these weights
are expressed, but it is more convenient if none are smaller
than 1. To accomplish this, the weight of the hydrogen
atom, being the smallest, was taken as 1, and all of the other
weights computed from it. On this basis the weight of oxygen
would be 15.87. An international congress of chemists agreed
to consider one-sixteenth the mass of the oxygen atom as the
unit. **An atomic weight, then, is a number showing how many times
heavier an atom is than one sixteenth of an oxygen atom.** In other
words, it is the ratio of the least mass of an element known
to form part of a molecule to one sixteenth of the mass of an
atom of oxygen.

27. Atomic weights of some common elements.

Oxygen = 16

Aluminum,	Al......... 27.10	Calcium,	Ca......... 40.00
Antimony,	Sb.........120.20	Carbon,	C.......... 12.00
Arsenic,	As......... 74.96	Chlorine,	Cl......... 35.46
Barium,	Ba.........137.40	Chromium,	Cr......... 52.00
Bismuth,	Bi.........208.00	Copper,	Cu......... 63.60
Bromine,	Br......... 79.92	Fluorine,	F.......... 19.00

Hydrogen,	H.......... 1.008	**Oxygen,**	**O**.......... **16.00**
Iodine,	I...........126.92	Phosphorus,	P........... 31.04
Iron,	Fe.......... 55.80	Potassium,	K.......... 39.10
Lead,	Pb.........207.10	Silicon,	Si.......... 28.30
Lithium,	Li.......... 6.94	Silver,	Ag.........107.88
Magnesium,	Mg......... 24.32	Sodium,	Na......... 23.00
Manganese,	Mn........ 54.93	Strontium,	Sr.......... 87.63
Mercury,	Hg.........200.60	Sulphur,	S.......... 32.07
Nickel,	Ni......... 58.68	Tin,	Sn........119.00
Nitrogen,	N.......... 14.01	Zinc,	Zn.......... 65.37

28. Molecular weight is a number showing how many times heavier a molecule of a substance is than one sixteenth the weight of an oxygen atom. It is equal to the sum of the atomic weights represented by the symbol for the molecule.

MEANING AND USE OF SYMBOLS, FORMULAS, AND EQUATIONS

In order to simplify the study of chemistry and relieve the student of the necessity of remembering countless numbers representing combining proportions and equivalent weights, it is necessary to introduce the exact use of symbols, formulas, and equations, without giving all of the reasons for their existence.

29. Full meaning of the symbol of an element.

The symbol of an element is a sign that stands for:

(1) That element.

(2) One atom of that element.

(3) A certain weight of the element. The number representing this weight is the same as the atomic weight of the element and may be found in any table of atomic weights.

Thus, S is a sign that stands for sulphur, for one atom of sulphur, and for thirty-two weights of sulphur.

30. Formula of a compound. The formula of a compound is a sign that stands for one molecule of that substance. It is made up of the symbols of the elements contained in the compound with a number below and at the right of each symbol indicating how many atoms of that element are contained in the molecule. A formula primarily tells the composition of the molecule, so we may also speak of the formula of an element.

The molecule of mercury has but one atom in it, so its formula is the same as the symbol Hg. The molecule of hydrogen has two atoms, and the formula is H_2. Other formulas of elements are N_2, O_2, Cl_2, As_4, and P_4.

31. Formulas of some common compounds.

H_2O, hydrogen oxide, or water.

CO_2, carbon dioxide, or carbonic acid gas.

MgO, magnesium oxide, or magnesia.

NaCl, sodium chloride, or common salt.

HCl, hydrogen chloride, hydrochloric acid, or muriatic acid.

HNO_3, hydrogen nitrate, or nitric acid.

H_2SO_4, hydrogen sulphate, sulphuric acid, or oil of vitriol.

32. Full meaning of the formula of a compound. This can best be shown by giving the exact meaning of some formula.

Full meaning of the formula H_2SO_4:

(1) H_2SO_4 is a sign that stands for sulphuric acid.

(2) It stands for one molecule of sulphuric acid.

(3) It stands for ninety-eight weights of sulphuric acid.

(4) It states that sulphuric acid is a compound of hydrogen, sulphur, and oxygen.

(5) It states that one molecule of sulphuric acid contains two atoms of hydrogen, one of sulphur and four of oxygen.

(6) It states that these elements are present in the proportion of 2 weights of hydrogen, 32 weights of sulphur, and 64 weights of oxygen.

33. To change the composition of a substance as shown by a formula to a percentage basis.

Example. To calculate the percentage composition of sulphuric acid from its formula, H_2SO_4.

The molecule contains two atoms of hydrogen or two weights, one atom of sulphur or thirty-two weights, and four atoms of oxygen or sixty-four weights.

$$
\begin{aligned}
2\,H &= 2 \\
S &= 32 \\
4\,O &= 64 \\
\hline
&\quad 98
\end{aligned}
$$

There are 98 weights in the molecule altogether; of these $\dfrac{2}{98}$ are

hydrogen, $\dfrac{32}{98}$ are sulphur, and $\dfrac{64}{98}$ are oxygen. It is only neces-
sary to reduce these fractions to the corresponding decimals
and multiply by 100 to get the percentages.

$$H = \frac{2}{98} = .0204, \text{ or } 2.04\%$$

$$S = \frac{32}{98} = .3265, \text{or } 32.65\%$$

$$O = \frac{64}{98} = .6531, \text{or } 65.31\%$$
$$\overline{100.00}$$

34. Exercise. Compute the percentage compositions of all
of the substances whose formulas are given in **31**.

35. Derivation of formulas from analysis. Having obtained an
exact analysis of a compound, if we divide each percentage by
the corresponding atomic weight, we shall obtain numbers
which will be proportional to the numbers of atoms of each
kind in the molecule. In the case of simple compounds these
numbers will all be simple multiples of the smallest. This in
any case will give us the simplest possible formula. It is pos-
sible that the real formula may be some multiple of the sim-
plest, and this can only be determined by ascertaining, at
least approximately, the molecular weight, which can be done
in several ways to be described later.

The analysis of water gives $H = 11.11\%$, $O = 88.89\%$;
dividing each of these two numbers by the corresponding atomic
weights gives $\dfrac{11.11}{1} = 11.11$, $\dfrac{88.89}{16} = 5.55$; 11.11 is twice as
large as 5.55; there must therefore be twice as many atoms of
hydrogen as of oxygen; the simplest formula would therefore
be H_2O.

The analysis of the gas formed by burning carbon in an excess
of oxygen gives $C = 27.27\%$, $O = 72.73\%$; dividing by the
atomic weights, $\dfrac{27.27}{12} = 2.272$, $\dfrac{72.73}{16} = 4.544$; 4.544 is just
twice as large as 2.272; there must be twice as many atoms of
oxygen as of carbon; the simplest formula must therefore
be CO_2.

36. Exercise. Derive the simplest formulas corresponding to the following analyses: hydrogen 2.74%, chlorine 97.26%; hydrogen 11.11%, oxygen 88.89%; hydrogen 17.63%, nitrogen 82.35%; hydrogen 25%, carbon 75%; lead 85.60%, sulphur 13.40%; calcium 51.10%, fluorine 48.90%; hydrogen 1.69%, nitrogen 22.22%, oxygen 76.19%; carbon 40%, hydrogen 6.67%, oxygen 53.33%.

37. Metals and non-metals. All the elements may be divided into two classes, metals and non-metals. In addition to the common elements like copper, lead, iron, tin, and silver, the student may remember that mercury, bismuth, and antimony are metals. Also that most of the elements whose names end in "um" are metals.

38. A binary compound is one containing only two elements. In naming a binary compound the name of the metal is placed first, unchanged, followed by the name of the non-metal with its name changed to an ending in "ide," *e. g.*, a compound of sodium and chlorine is called sodium chloride; or of iron and oxygen, iron oxide, etc. While almost any element may form a binary compound with any other element, by far the most common compounds are those of the metals with the non-metals.

Where both of the elements are non-metals, the name of either may be placed first, followed by the name of the other with an ending in "ide," *e. g.*, hydrogen nitride or nitrogen hydride.

COMBINING POWER, OR VALENCE

39. Atoms have different capacities for combining. As we have just shown, the formula of a compound may be determined from the analysis, together with the molecular weight and the atomic weights of the elements concerned (**35**).

The formulas of all the binary compounds have been determined; and from an inspection of them it appears that the atoms of the various elements have different powers or capacities of holding each other in combination in the molecules.

40. Combining power, or valence, is the power that an atom has of combining with other atoms to form molecules. This power

is commonly measured by the number of hydrogen atoms, or their equivalent, with which a given atom can combine.

Combining Power of the Elements by Groups

The combining powers are very symmetrically arranged according to groups.

The elements in group one have a power of 1.

The elements in group two have a power of 2.

The elements in group three have a power of 3.

The elements in group four have a power of 4 (lead and tin also have a power of 2).

The elements in group five have powers of 3 and 5.

The elements in group six have powers of 2, 4, and 6, except oxygen, which has only 2.

The elements in group seven have powers of 1, 3, 5, and 7.

The elements in group eight have powers of 2 and 3.

Derivation of Formulas of Binary Compounds from the Known Combining Powers of the Elements

41. Almost any two elements can combine to form a binary compound. **The total valence, or combining power, of the atoms of any one kind forming a molecule of a binary compound is the least common multiple of the two combining powers concerned.**

In other words, there must be atoms enough of the first kind present to give a total valence equal to that of one or more atoms of the second kind. If this valence is the least possible one that gives equivalent combining powers, the resulting formula is the simplest one possible. **It must be remembered that the simplest formula is not necessarily the correct one.** The true formula may be a multiple of the simplest (**382**).

In cases where an element has several combining powers the one to be used, unless stated to the contrary, is the lowest.

Sodium chloride. Sodium, being in the first group, has a power of 1, and one atom of it will therefore exactly combine with one atom of chlorine, which is in the seventh group, but has a low common combining power of 1. The formula would be NaCl, sodium chloride.

Magnesium chloride. Magnesium, in the second group with a power of 2, will combine with two atoms of chlorine, giving the formula $MgCl_2$, magnesium chloride.

Aluminum chloride. Aluminum, in the third group, with a power of 3, would combine with three atoms of chlorine, giving the formula $AlCl_3$, aluminum chloride.

Carbon chloride. The formula of a compound of carbon and chlorine would be CCl_4.

Aluminum oxide. The formula of a compound of aluminum and oxygen would be Al_2O_3, for the least common multiple of the two valences would be 6, and it takes two aluminum atoms to give an equivalent power. Oxygen always has a power of 2 and it will therefore take three to give a total power of 6.

The subnumbers in the formula are ordinarily the same as the two valences reversed. If one is divisible by the other, the simplest ratio is taken in the reversed order, *e. g.*, carbon has a power of 4 and oxygen of 2; the formula is not C_2O_4 but CO_2.

42. Prefixes. When two elements form several different binary compounds, it is customary to distinguish between them by placing the prefixes mon-, di-, tri-, tetra-, pent-, etc., before the name of the variable element. Thus SO_2 is sulphur dioxide, SO_3 is sulphur trioxide, P_2O_3 is phosphorus trioxide, and P_2O_5 is phosphorus pentoxide.

Remember always that formulas are not originally derived from valence, but valence from formulas. And that the theory of valence is taught only to relieve the student of the necessity of remembering the combining proportions of the elements in thousands of compounds.

43. Exercise. Give the formulas and names of all of the binary compounds of the metals with the non-metals.

44. Chemical equivalence. A quantity of one element is said to be equivalent (equi-valent) to a certain quantity of another element when there are enough atoms of each present to give the same total combining power.

One atom of sodium is equivalent to one atom of potassium.

Two atoms of sodium are equivalent to one atom of magnesium.

Two atoms of magnesium are equivalent to one atom of carbon.

Three atoms of zinc are equivalent to two atoms of aluminum.

The term "atom" is used in the sense of a certain number of weights. Thus, "three atoms of zinc" means three times sixty-five weights of zinc, and "two atoms of aluminum" means two times twenty-seven weights of aluminum.

45. The number of grams of any one element equivalent to a certain number of grams of any other element. How many grams of aluminum are equivalent to 10 g. of zinc? Two atoms of aluminum are equivalent to 3 atoms of zinc. That is, 54 weights of aluminum are equivalent to 3 atomic weights of zinc. $3 \times 65 = 195$ weights. One weight of zinc would therefore be equivalent to $\dfrac{1}{195}$ of 54 weights of aluminum, and 10 weights of zinc would be equivalent to $10 \times \dfrac{54}{195}$ weights of aluminum.

NOTE that in all questions of this sort that occur in chemistry there are two important chemical equivalent numbers concerned. **The given weight is multiplied by a fraction in which one of these numbers is the numerator and the other the denominator.** The **numerator** is always the chemical equivalent number corresponding to the element or substance whose weight is desired.

Again: 10 g. of carbon are equivalent to how many grams of nitrogen?

Three carbon atoms are equivalent to 4 nitrogen atoms.

Thirty-six weights of carbon are equivalent to 56 weights of nitrogen.

The question concerns nitrogen. The answer is $\dfrac{56}{36} \times 10$ g.

46. Exercise. Give the chemical equivalence between every pair of elements on the chart. State in fractional form how many grams of any one element are equivalent to 10 g. of any other element. **This should be done mentally,** a chart giving the atomic weights being in sight.

Questions

1. State the law of definite weight (23); of multiple proportions (24).
2. Outline the atomic hypothesis of Dalton (25).
3. **What is an atomic weight?** Upon what is it based? (26).
4. What is a molecular weight? (28). Give the full meaning of any symbol (29).
5. **What is the formula of a compound?** (30); of an element? Give the formulas of seven compounds with the names of the substances for which they stand (31).
6. **Give the full meaning of each of the above formulas (32).**
7. **Calculate the percentage composition of a substance, corresponding to its formula (33).** Derive the simplest formula from the analysis of a compound (35).
8. **Name all of the metals; the non-metals (37).** What is a binary compound? (38).
9. Name the compounds of each of the metals with each of the non-metals.
10. What is valence? (40). **Give the valences of the elements in groups (40).**
11. What relation do the sub-numbers bear to the valences of the combining elements in a binary compound? (41). **Give the formulas of the compounds of each metal with each non-metal (41).**
12. How are prefixes used? (42). **What is meant by chemical equivalence? (44).**
13. **10 g. of any element are equivalent to how many grams of any other element? (45). How many grams of any element are equivalent to 10 g. of any other element? (45).**
14. **How can you write the expression for the answer to the above questions at once? (45).**

CHAPTER IV

EQUATIONS

47. Least number of molecules involved. A **reaction** is a chemical change. A **reagent** is any substance capable of entering into a reaction.

When the quantity and chemical composition of all the substances involved in a reaction have been determined by experiment, it is possible to ascertain the relative numbers of molecules of the different substances concerned by dividing each weight by the molecular weight of the corresponding substances. This will give numbers proportional to the numbers of different molecules involved. The smallest possible whole numbers corresponding will represent the least possible numbers of molecules of the substances capable of entering into that reaction.

48. A chemical equation, then, is one on the left-hand side of which are placed the formulas of the molecules of the substances used, and on the right-hand side are placed the formulas of the molecules of the substances formed. A number is placed before each formula indicating the least possible number of molecules of that substance capable of taking part in that reaction.

An equation can never be a complete description of a reaction, for it only tells the nature and proportions of the substances involved. Besides these facts a complete description should state the exact conditions under which that particular reaction takes place, especially with regard to the temperature, pressure, and the concentrations of the substances involved.

Since an equation is to represent the smallest possible quantity of actual material that can take part in a reaction, it is apparent that the symbols used must represent molecules. This is simple enough in the case of compounds, but in the case of elements there is considerable uncertainty. The mo-

lecular weights of many of the elements are unknown; several have two atoms in the molecule, and some have more than two.

For the sake of uniformity we state that the elementary substances, **oxygen, hydrogen, nitrogen, fluorine, chlorine, bromine, and iodine,** have **two atoms in the molecule** and that when they appear **by themselves,** *i. e.,* **not in a compound,** they should be written O_2, H_2, N_2, F_2, Cl_2, Br_2, and I_2.

On account of the uncertainty, and for uniformity in writing equations, the pupil may **assume** that all other elements have but one atom in the molecule.

49. Construction of equations. Experiment shows that 11.11 g. of hydrogen exactly unite with 88.89 g. of oxygen to form 100 g. of water. The molecular weight of hydrogen is 2, the molecular weight of oxygen is 32, and the molecular weight of water is 18; dividing the combining weights by the corresponding molecular weights, we have:

$$\frac{11.11}{2} = 5.55; \quad \frac{88.89}{32} = 2.78; \quad \frac{100.0}{18} = 5.55.$$

The smallest whole numbers proportional to these are 2, 1, and 2. There are therefore two molecules of hydrogen, one of oxygen, and two of water. The resulting equation would be:

$$2 H_2 + O_2 = 2 H_2O.$$
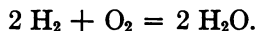
Again, we have the case of aluminum burning in oxygen. Experiment shows that 26.47 g. of aluminum exactly combine with 23.53 g. of oxygen to form 50 g. of aluminum oxide. Dividing as before by the corresponding molecular weights, we have:

$$\frac{26.47}{27} = .9804; \quad \frac{23.53}{32} = .735; \quad \frac{50.0}{102} = .4901.$$

It appears from inspection that these numbers are proportional to 2, 1½, and 1; the smallest whole numbers corresponding would be 4, 3, and 2. The equation would therefore be:

$$4 Al + 3 O_2 = 2 Al_2O_3.$$
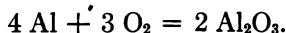
50. Equations showing formation of binary compounds. With a knowledge of valence we can in many cases write the equation

showing the formation of a binary compound at once without a knowledge of the combining proportions obtained by experiment.

When magnesium burns in oxygen, magnesium oxide is formed. The theory of valence tells us that its formula is MgO; it is evidently made from one atom of oxygen and one atom of magnesium. The atomic equation would be:

$$Mg + O = MgO.$$
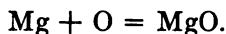
The smallest quantity of oxygen which we can use, however, is one molecule, which is O_2; **we must therefore use twice the quantity of magnesium and get two molecules of the product.** Rewriting the equation, we have:

$$2\,Mg + O_2 = 2\,MgO.$$
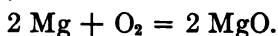
When phosphorus is burned in an excess of oxygen the highest possible oxide is formed. This is phosphorus pentoxide, P_2O_5. It is evidently formed by the combination of two atoms of phosphorus and five atoms of oxygen. The atomic equation would be:

$$2\,P + 5\,O = P_2O_5.$$

It is again evident that we shall have to use twice the quantity of material and get twice as many molecules of the product. Rewriting the equation, we have:

$$4\,P + 5\,O_2 = 2\,P_2O_5.$$
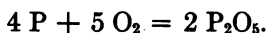
It should be recognized at once that when the product contains an odd number of atoms of the elements oxygen, hydrogen, nitrogen, fluorine, chlorine, bromine, or iodine, the quantities must be doubled, and the equation written correctly at once.

51. Full meaning of a chemical equation. It is important that the student should constantly realize that equations are derived from facts and not facts from equations. The mere juggling with symbols and formulas is not going to produce a fact. When the fact is once known it may generally be expressed by an equation. The full meaning of a chemical equation may best be illustrated by an example:

$$4\,Al + 3\,O_2 = 2\,Al_2O_3.$$
$$108 \qquad 96 \qquad\ \ 204$$
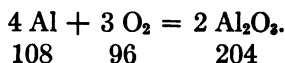
(1) It makes a qualitative statement: aluminum combines with oxygen to form aluminum oxide.

(2) It tells the number of molecules concerned: four atoms (assumed to be the same as molecules) of aluminum exactly unite with three molecules of oxygen to form two molecules of aluminum oxide.

(3) It states the exact proportions by weight of the substances involved: 108 weights of aluminum exactly unite with 96 weights of oxygen to form 204 weights of aluminum oxide.

(4) If the weight of one of the reacting substances is given in any denomination whatever, the weights of all the others may be written at once; for, if 108 g. of aluminum combine with 96 g. of oxygen, 1 g. would combine with 1/108 as much, or $\frac{96}{108}$ g., and 10 g. of aluminum would exactly combine with $\frac{96}{108} \times 10$ g. of oxygen. Exactly the same argument would give the quantity of aluminum oxide formed by 10 g. of aluminum as $\frac{204}{108} \times 10$.

If we were required to find how many grams of aluminum and how many grams of oxygen would be required to form 10 g. of aluminum oxide, the argument would be similar.

Since 204 g. of aluminum oxide are formed from 108 g. of aluminum, 1 g. would be formed by $\frac{1}{204}$ as much, or by $\frac{108}{204}$ g., and 10 g. would be formed from $\frac{108}{204} \times 10$ g. In the same way the quantity of oxygen would be $\frac{96}{204} \times 10$ g.

52. Short method. It should be noted that in every example the known weight in grams is multiplied by a certain fraction, the numerator of which is the combining weight of the substance whose real weight is desired, and the denominator the combining weight of the substance whose real weight is given.

Illustration. How many grams of phosphorus would combine with 10 g. of oxygen, and how many grams of phosphorus pentoxide would be formed?

$$4P + 5O_2 = 2P_2O_5.$$
$$124 \quad 160 \quad\quad 284$$
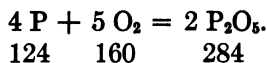
$\dfrac{124}{160} \times 10$ g. would combine with 10 g. of oxygen and form

$\dfrac{284}{160} \times 10$ g. of phosphorus pentoxide.

Questions

1. What is a reaction? a reagent?   How is it possible to derive an equation from the weights of the reacting substances? (47).
2. Define the term "chemical equation."   Does an equation represent all of the facts? (48).
3. What elements are known to have two atoms in the molecule? (48).
4. Write equations showing the formation of all possible binary compounds of metals with non-metals (50).
5. Give the full meaning of any equation (51).
6. How many grams of any element would form 10 g. of a binary compound?   10 g. of any element will form how many grams of a binary compound? (52).

CHAPTER V

RADICALS

53. Electrolytic dissociation. When acids, bases, and salts are dissolved in water some of the molecules so dissolved are broken up by the water into at least two parts, one of the parts being hydrogen or a metal and the other the rest of the molecule. This process is known as electrolytic dissociation (191).

54. Ions. Each part carries a charge of electricity, that on the hydrogen or the metal being positive electricity and that on the rest of the molecule being negative electricity. Atoms or groups of atoms existing in solution and carrying electric charges are called **ions**. When sodium chloride is dissolved in water it is partially split into sodium atoms each charged with positive electricity and chlorine atoms each charged with negative electricity, the quantity of the positive charge being exactly equal to that of the negative charge. A substance which is dissociated into ions in solution is known as an **electrolyte** (203).

55. Designation of ions. When it is desirable to indicate electrolytic dissociation in an equation, plus or minus signs are placed above and at the right of each symbol or group of symbols indicating the number of electric charges carried: *e. g.*, Na^+; Ba^{++}; Cl^-; SO_4^{--}; Al^{+++}. The number of charges corresponds to the valence of the element:

$$HCl \text{ in solution} \rightleftharpoons H^+ + Cl^-.$$
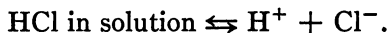
56. Dissociation of compounds containing more than two kinds of atoms in the molecule. Compounds containing more than two kinds of atoms in the molecule, if they are subject to electrolytic dissociation at all, are broken up into one or more positive ions and one or more negative ions. Thus:

$$H_2SO_4 \text{ dissolved} \leftrightarrows H^+ + H^+ + SO_4^{--};$$
$$\text{and } Al_2(SO_4)_3 \text{ dissolved} \leftrightarrows Al^{+++} + Al^{+++}$$
$$+ (SO_4)^{--} + (SO_4)^{--} + (SO_4)^{--}.$$
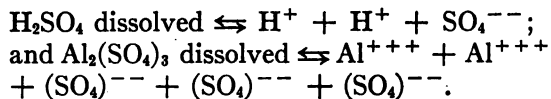
57. Radicals. A radical is an atom or group of atoms that enters various reactions as a whole. Examples: H; Na; Cl; SO_4; NO_3.

Basic and acid radicals. Two bodies charged with unlike kinds of electricity attract each other, and two charged with the same kind repel. If two conductors, connected with the poles of a battery or other source of electricity, be immersed in a solution containing ions, the conductor which is charged positively by the battery attracts the negative ions, and repels the positive ions. The one charged negatively attracts the positive ions and repels the negative. The conductors so immersed are known as **electrodes.** Those atoms which, as ions, drift toward the negative electrode are called **basic** or **positive radicals,** those which drift toward the positive electrode are called **acid** or **negative radicals.** The non-metals and groups of non-metals constitute the acid radicals.

58. Valence of radicals. Radicals may be considered as having valences exactly like the elements themselves, and to unite with each other to form compounds in a similar way, basic radicals uniting, as a general rule, with acid radicals.

59. Names of radicals. The names of the basic radicals are essentially the same as the names of the metals, the names of the acid radicals are the same as the names of the second part of the compounds they form with the basic radicals. Thus, Na is the symbol of the sodium radical, and SO_4 is the symbol of the **sulphate radical.** Na_2SO_4 is the formula of a compound containing these two radicals, and it is known as sodium sulphate (**104**).

60. Radicals having two different valences. If a radical has two different valences, it is evident that it will form two different classes of compounds; and it is therefore necessary to assign two different names to it. Thus iron has valences of 2 and 3. The iron radical with a valence of 2 is called "**ferrous**" and that with a valence of 3 is called "**ferric.**" Copper with a valence of 1 is called "**cuprous**" and with a valence of

2 is called "cupric." In general, when a metallic radical has two valences, the name of the one having the lower valence ends in "ous" and the higher in "ic" (105).

LIST OF SOME COMMON RADICALS

61. The following list gives some of the more common radicals. These are sufficient for purposes of drill in giving formulas and names of compounds. They should be thoroughly memorized the first time they are met, preferably in class. The derivation of these as well as other radicals will be given later. The student will soon learn to recognize the names and valences of radicals in the formulas of compounds he has never seen before.

Basic or Positive Radicals	Acid or Negative Radicals
Valence of 1	*Valence of 1*
H, Hydrogen.	$C_2H_3O_2$, Acetate.
Na, Sodium.	Br, Bromide.
K, Potassium.	ClO_3, Chlorate.
NH_4, Ammonium.	Cl, Chloride.
Aġ, Silver.	OH, Hydroxide.
Hg, Mercurous.	I, Iodide.
Cu, Cuprous.	NO_3, Nitrate.
Valence of 2	*Valence of 2*
Mg, Magnesium.	CO_3, Carbonate.
Ca, Calcium.	O, Oxide.
Zn, Zinc.	SO_4, Sulphate.
Ba, Barium.	S, Sulphide.
Hg, Mercuric.	*Valence of 3*
Cu, Cupric.	PO_4, Ortho-phosphate.
Fe, Ferrous.	$Fe(CN)_6$, Ferricyanide.
Pb, Lead.	$Fe(CN)_6$, Ferrocyanide.
Valence of 3	
Al, Aluminum.	
Fe, Ferric.	

FORMULAS OF COMPOUNDS CONTAINING MORE THAN TWO ELEMENTS

Combinations of Radicals

62. In general, basic radicals combine with acid radicals. In a formula of a compound the total valence of all the basic radicals must be equal to the total valence of all of the acid radicals. If the compound were formed in solution, the total quantity of positive electricity from the basic ions would exactly equal the total quantity of negative electricity furnished by the acid ions.

When it is necessary to represent a compound radical as occurring several times in a formula, the whole radical is placed in parentheses with a number below and at the right showing how many times.

The name of the compound is formed by simply putting together the two names of the radicals, placing that of the basic radical first.

It is quite possible for the total valence of a given kind to be furnished by two or more different radicals either basic or acid, but for the present it will be assumed that all the basic or acid radicals in a formula are of the same kind.

To illustrate, consider the possible formulas resulting from combining each of the following basic radicals with each of the acid radicals. The valence of the radical is indicated by dots placed above:

Basic Radicals	Acid Radicals
H·	Cl·
Na·	NO₃·
Ba··	SO₄··
Al···	PO₄···
	Fe(CN)₆····

(a) In hydrogen compounds:

H, having a valence of 1, the number of H's will be the same as the valence of the acid radical.

HCl, hydrogen chloride.

HNO_3, hydrogen nitrate.

H_2SO_4, hydrogen sulphate.

H_3PO_4, hydrogen ortho-phosphate.

$H_4Fe(CN)_6$, hydrogen ferrocyanide.

(b) **Also in sodium compounds,** the sodium having a valence of 1, the formulas are simple:

NaCl, sodium chloride.

$NaNO_3$, sodium nitrate.

Na_2SO_4, sodium sulphate.

Na_3PO_4, sodium ortho-phosphate.

$Na_4Fe(CN)_6$, sodium ferrocyanide.

(c) **Barium compounds:**

$BaCl_2$, barium chloride. Here two chlorine radicals were necessary to give a total valence equal to that of barium.

$Ba(NO_3)_2$, barium nitrate. Here again two nitrates were necessary.

$BaSO_4$, barium sulphate. One sulphate, having a valence of 2, was at once equivalent to one barium.

$Ba_3(PO_4)_2$, barium ortho-phosphate. Here we must have enough barium radicals to be equivalent to some number of phosphate radicals. Three bariums give a total valence of 6, and two phosphate radicals give the same valence.

$Ba_2Fe(CN)_6$, barium ferrocyanide. Two bariums are at once equivalent to one ferrocyanide radical.

(d) **Aluminum compounds:**

$AlCl_3$, aluminum chloride.

$Al(NO_3)_3$, aluminum nitrate.

$Al_2(SO_4)_3$, aluminum sulphate. Two aluminum radicals give a total valence of 6, which is the total valence of three sulphate radicals.

$Al_4(Fe(CN)_6)_3$, aluminum ferrocyanide. The two valences concerned are 3 and 4. The least common multiple of these two numbers is 12. It takes four 3's to make 12, therefore four Al's. Three ferrocyanide radicals also give 12.

In general if M represents a radical with a valence of x and N represents a radical with a valence of y, the formula would be M_yN_x.

That is, the subnumbers are the valences reversed.

In case one valence is divisible by the other, the subnumbers are the least ratio of the valences reversed.

M with a valence of x and N with a valence of $2x$ would give the formula M_2N.

IMPORTANT CLASSES OF COMPOUNDS
Acids

63. An acid is a substance that gives hydrogen ions in solution. It is generally sour to the taste and turns blue litmus paper red. It consists of the hydrogen radical joined to any acid radical except O or OH. It reacts with a base or basic oxide to form water and a salt.

Examples: $HC_2H_3O_2$; HBr; HNO_3; H_2SO_4; H_3PO_4; $H_4Fe(CN)_6$.

Bases

64. A base is a compound that gives hydroxide ions in solution. It consists of any basic radical except H, joined to the radical OH. It reacts with an acid to form water and a salt.

Examples: $NaOH$; KOH; NH_4OH; $Mg(OH)_2$; $Al(OH)_3$; $Fe(OH)_3$.

Alkalies

65. An alkali is a base that is highly dissociated in solution, giving a large quantity of hydroxide ions.

It turns red litmus paper blue, and is soapy to the taste and feeling.

Examples: $NaOH$; KOH; NH_4OH; $Ca(OH)_2$; $Sr(OH)_2$; $Ba(OH)_2$.

Salts

66. A salt is a compound formed together with water when an acid acts on a base or a basic oxide.

It always consists of a basic radical other than H, joined to an acid radical other than O or OH.

Examples: $NaCl$; Na_2SO_4; Na_3PO_4; $CaCl_2$; $CaSO_4$; $Ca_3(PO)_2$.

Oxides

67. An oxide is a compound of an element with oxygen.

A basic oxide is one that unites with an acid to form water and a salt. Most of the oxides of the metals are basic oxides.

Examples: Na_2O; K_2O; MgO; BaO; HgO; Al_2O_3; FC_2O_3.

68. An alkaline oxide is a basic oxide that unites with water to form an alkali.

Examples: Na_2O; K_2O; CaO; SrO; BaO.

69. An acidic oxide is one that unites with a base to form water and a salt. Most of the oxides of the non-metals are acidic oxides.

Examples: CO_2; SiO_2; SO_2; SO_3; P_2O_3; P_2O_5.

70. An acid anhydride is an acidic oxide that unites with water to form an acid.

Examples: SO_2; SO_3; N_2O_3; N_2O_5; P_2O_5.

71. Exercise. Give the names of the compounds of each of the basic radicals with each of the acid radicals and state to which of the above classes the resulting compound belongs. Thus: hydrogen acetate, acid; sodium hydroxide, base and alkali; calcium sulphate, salt; cupric oxide, basic oxide; sodium oxide, basic and alkaline oxide; ferric hydroxide, base.

NOTE. H_2O and HOH are both formulas for water. Water is neither an acid nor a base, for it furnishes an equal quantity of hydrogen and hydroxide ions.

Questions

1. What is electrolytic dissociation? (**53**); an ion? (**54**). What ions does sodium chloride form in water solution? (**54**). How are ions designated in an equation? (**55**). What is an electrolyte? (**54**). What is a radical? (**57**); a basic or positive radical? an acid or negative radical? (**58**).
2. How are radicals having different valences named? (**60**).
3. Give the complete list of common radicals in groups (**61**).
4. Give the formulas and names of the compounds of each of the basic radicals with each of the acid radicals. This should require not more than ten minutes (**62**).
5. What is an acid? (**63**). Give the formulas and names of ten acids.
6. What is a base? (**54**). Give the formulas and names of ten.
7. What is a salt? (**66**). Give the formulas and names of ten.
8. What is an alkali? (**65**). Give the formulas of five.
9. What is a basic oxide? (**67**). Give the formulas and names of ten.
10. What is an alkaline oxide? (**68**). Give the formulas and names of five.
11. What is an acidic oxide? (**69**). Give the formulas and names of five.
12. What is an acid anhydride? (**70**). Give the formulas and names of five.
13. What ion does an acid always furnish in solution? (**63**). What ion is characteristic of a base? (**64**).

CHAPTER VI

SOME REACTIONS RESULTING IN THE FORMATION OF SALTS

72. Reversible reactions. In one sense all reactions are reversible. The reaction proceeds until a definite condition of equilibrium is attained—that is, until the tendency of the products to reform the factors is just equalled by the tendency of the factors to form the products (235):

$$ZnS + 2\,HCl \leftrightarrows ZnCl_2 + H_2S.$$
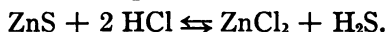
73. Change in direction of reaction. When a condition of equilibrium has been reached any change in the quantity of any one of the factors or products is balanced by a change in some other. In the above equation, if the concentration of the HCl be increased, more of the ZnS will be dissolved; if it be decreased, more zinc sulphide will be formed.

74. Completed reactions. If one or more of the products of a reaction be completely removed from its immediate sphere of formation, the reaction will proceed until one or more of the reacting substances is entirely transformed. This may happen in several different ways:

(*a*) **One of the products may be a gas,** in which case it is set free and escapes:

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$
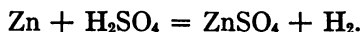
(*b*) **One of the products may be an insoluble or undissociated substance,** in which case it is incapable of reversing the reaction, and therefore the reaction goes on to virtual completion:

$$ZnSO_4 + BaCl_2 = \overline{BaSO_4} + ZnCl_2;$$
$$NaOH + HCl = \overline{NaCl} + HOH.$$
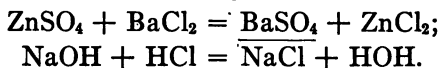
(*c*) **One of the possible products may immediately enter a new reaction with some other substance present,** thereby allowing the original reaction to go to completion.

In the reaction of hydrogen sulphide upon zinc chloride, the reaction is incomplete on account of the formation of HCl,

which tends to reverse it. If some ammonium hydroxide be present, the HCl is neutralized as fast as formed and the reaction goes to completion (234).

75. Solution pressure. All metals when placed in liquids tend to send off positive ions into solution. The tendency of a metal to send off these ions is known as its **solution pressure.** It is very different for different metals. Sodium, magnesium, and zinc have high solution pressures, while copper, silver, and gold have low solution pressures. If a metal with a high solution pressure be placed in a solution of a salt of a metal with a low solution pressure, ions from the first will enter the solution and an equivalent amount of the second metal will be precipitated. Hydrogen may be considered as having a solution pressure similar to that of metals (**194**).

FIRST METHOD OF MAKING SALTS ·

Action of a Metal on an Acid

76. If a metal having a higher solution pressure than hydrogen be placed in an acid, ions from the metal enter the solution and an equivalent amount of hydrogen is set free in the gaseous form. **In other words, the metal takes the place of an equivalent quantity of the hydrogen of the acid.** If the metal has a lower solution pressure than hydrogen, no action will take place. Also, if there is an oxidizing agent present, the hydrogen will be oxidized to water and will not appear in the gaseous condition.

If it were possible to prevent the escape of the hydrogen, the reaction would go on until there were enough hydrogen ions in solution to prevent the formation of any more metal ions, and a condition of equilibrium would be established.

In the case of zinc in dilute sulphuric acid, the hydrogen escapes, and zinc and sulphate ions are left in solution. The reaction goes on until the zinc is all dissolved, the acid all used up, or the solution becomes so saturated with the products of the reaction that no more can enter the liquid.

If the liquid be evaporated, the zinc ions unite with the acid sulphate ions and a salt known as zinc sulphate crystallizes out:

$$Zn + H_2SO_4 = Zn^{++} + SO_4^{--} + H_2.$$
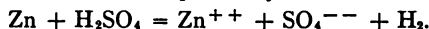
77. Exercise. Write equations showing the formation of the following indicated twenty-five salts by the above method—twenty-five equations:

Na$^{\cdot}$	Cl$^{\cdot}$
K$^{\cdot}$	NO$_3$$^{\cdot}$
Mg$^{\cdot\cdot}$	SO$_4$$^{\cdot\cdot}$
Ba$^{\cdot\cdot}$	PO$_4$$^{\cdot\cdot\cdot}$
Al$^{\cdot\cdot\cdot}$	Fe(CN)$_6$$^{\cdot\cdot\cdot\cdot}$

Examples:

(a) **Sodium chloride.** First, put down in the form of an equation the correct formulas of the molecules of all the substances concerned:

$$Na + HCl = NaCl + H_2.$$

Now the student should recognize by inspection the least common multiple of all of the positive valences concerned. In this equation they would be 1, 1, 1, and 2; the least common multiple would be 2. Coefficients are now placed before each formula so that the total positive valence in each substance will be the same.

The equation then becomes

$$2\,Na + 2\,HCl = 2\,NaCl + H_2.$$
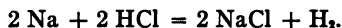
This least common multiple may be called the **equivalent number** for the equation.

A few other illustrations will make it plain.

(b) **Magnesium phosphate.** To indicate the formation of magnesium phosphate we should have to use Mg, H_3PO_4, and get $Mg_3(PO_4)_2$ and H_2.

Here we recognize the equivalent number as the least common multiple of 2 and 3, or 6.

We can write at once, then

$$3\,Mg + 2\,H_3PO_4 = Mg_3(PO_4)_2 + 3\,H_2.$$
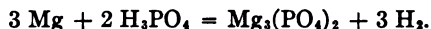
(c) **Aluminum ferrocyanide.** Again, suppose that we wanted to indicate the possible formation of aluminum ferrocyanide, $Al_4(Fe(CN)_6)_3$, we should have to use Al with the acid $H_4Fe(CN)_6$; here we have the numbers 3 and 4, to give the least common multiple, which is 12.

The equation therefore becomes

$$4\,Al + 3\,H_4Fe(CN)_6 = Al_4(Fe(CN)_6)_3 + 6\,H_2.$$
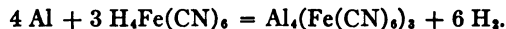
SECOND METHOD OF MAKING SALTS

78. The action of a basic oxide on an acid. In this kind of reaction the oxygen of the oxide unites with the hydrogen of the acid to form water, leaving the basic radical of the oxide to unite with the acid radical of the acid when the solution is evaporated. The method can only be used for the preparation of soluble salts.

79. Exercise. Indicate by equations the formation of the same twenty-five salts by this method (77).

For example, suppose that we wished to show the formation of sodium phosphate by this method. It would be made by the action of sodium oxide on hydrogen ortho-phosphate:

$$Na_2O + H_3PO_4 = Na_3PO_4 + H_2.$$
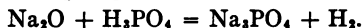
From an inspection of the formulas involved it appears that the equivalent number for this equation is 6.

The complete equation would therefore be

$$3 Na_2O + 2 H_3PO_4 = 2 Na_3PO_4 + 3 H_2.$$
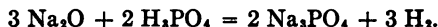
The total positive valence indicated by 3 Na_2 is 6; also the total positive valence of 2 H_3 is 6, and the two compounds are therefore equivalent.

THIRD METHOD OF MAKING SALTS

80. The action of a base on an acid. In this case the hydroxide of the base unites with the hydrogen of the acid, forming water. This leaves the basic radical of the base to unite with the acid radical of the acid to form a salt, which is left in the solid form when the water is allowed to evaporate.

This type of reaction is one that goes virtually to completion for the reason that water is almost completely undissociated and therefore cannot reverse the reaction (191).

For example, sodium hydroxide gives the ions Na^+ and OH^-, and hydrochloric acid gives the ions H^+ and Cl^-. When solutions of these two reagents are mixed in exact proportions the hydrogen ions unite with the hydroxide ions forming water, leaving the sodium and chlorine ions in solution:

$$Na^+ + OH^- + H^+ + Cl^- = HOH + Na^+ + Cl^-.$$
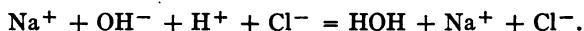
81. Exercise. Represent by equations the formation of the same twenty-five salts by this method (77).

Sodium sulphate would be made from sodium hydroxide and sulphuric acid:

$$NaOH + H_2SO_4 = Na_2SO_4 + HOH.$$

It is apparent that the equivalent number for this equation is 2. The equation would therefore become

$$2 NaOH + H_2SO_4 = Na_2SO_4 + 2 HOH.$$
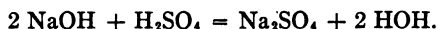
It is a little better for the sake of uniformity to write HOH for water in this reaction rather than H_2O.

In order to make aluminum sulphate, we should have to use aluminum hydroxide and sulphuric acid, and we should get aluminum sulphate and hydrogen hydroxide, or water:

$$Al(OH)_3 + H_2SO_4 = Al_2(SO_4)_3 + HOH.$$
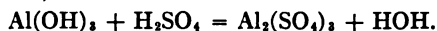
The numbers involved are 3, 2, and 1; the equivalent number would therefore be 6. The equation becomes

$$2 \, Al(OH)_3 + 3 \, H_2(SO_4) = Al_2(SO_4)_3 + 6 \, HOH.$$
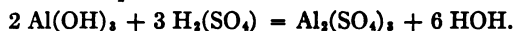
FOURTH METHOD OF MAKING SALTS

82. The action of an acid on a salt of a more volatile acid. In this reaction the hydrogen of the acid unites with the acid radical of the salt to form another acid, which is either unstable and breaks up into volatile gaseous compounds at once, or evaporates as an acid either with or without the application of heat, leaving the acid radical of the original acid combined with the basic radical of the salt. On account of the escape of the volatile acid from the solution the reaction goes on to completion.

Carbonic acid, or hydrogen carbonate, H_2CO_3, is one of the most unstable and volatile acids; therefore almost any acid will decompose a carbonate. Sulphuric and phosphoric acids are very stable and non-volatile. Almost any salt other than a sulphate or a phosphate, treated with sulphuric acid, gives rise to the formation of a sulphate and another acid which evaporates with or without heat.

For the sake of uniformity at the start, the student may best use the carbonate of the required metal with the acid.

83. Exercise. Show by equations the formation of the same twenty-five salts by the action of acids on carbonates (77).

In order to make sodium phosphate, we should have to use sodium carbonate with phosphoric acid, and we should get sodium phosphate and carbonic acid. Since H_2CO_3 is unstable it should always be written $\overline{H_2O + CO_2}$.

$$Na_2CO_3 + H_3PO_4 = Na_3PO_4 + H_2CO_3.$$
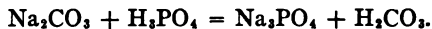
The numbers involved here are 2 and 3; the equivalent number is 6. Note that the molecule of carbonic acid contains one molecule of water and one molecule of carbon dioxide, and that in the finished equation there will always be the same number of molecules of each. The finished equation is, therefore,

$$3 \, Na_2CO_3 + 2 \, H_3PO_4 = 2 \, Na_3PO_4 + \overline{3 \, H_2O + 3 \, CO_2};$$
$$CaCO_3 + 2 \, HCl = CaCl_2 + \overline{H_2O + CO_2}.$$
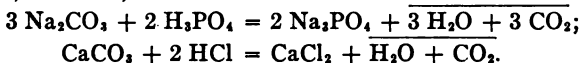
84. Classes of acids. In order that the student may intelligently make use of this kind of reaction, it is important that he should have some idea of the relative degrees of stability or volatility of some of the more common acids. It is therefore desirable that he should recognize three classes of acids and be familiar with a few examples in each class.

(a) **First class.** Acids that are very stable and non-volatile:

H_2SO_4, hydrogen sulphate, or sulphuric acid.

H_3PO_4, hydrogen ortho-phosphate, or ortho-phosphoric acid.

(b) **Second class.** Acids that are easily volatile but of sufficient stability to be prepared in the free condition.

HNO_3, hydrogen nitrate, or nitric acid.

HCl, hydrogen chloride, or hydrochloric acid.

$HC_2H_3O_2$, hydrogen acetate, or acetic acid.

(c) **Third class.** Acids that are so unstable that they decompose, the moment they are formed, into water and oxides of non-metals.

H_2CO_3, hydrogen carbonate, or carbonic acid. Decomposes into H_2O and CO_2.

H_2SO_3, hydrogen sulphite, or sulphurous acid. Decomposes into H_2O and SO_2.

HNO_2, hydrogen nitrite, or nitrous acid. Decomposes into H_2O and N_2O_3.

Two acids in the same class are not supposed to be involved in the same reaction.

FIFTH METHOD OF MAKING SALTS

85. The mixing of two solutions, one of which contains the basic radical and the other the acid radical of an insoluble compound.

In this case the insoluble compound separates at once as a precipitate and may be filtered off. If the two substances have been mixed in chemically equivalent proportions, the filtrate may be evaporated and the other compound obtained. Either of the two compounds formed may be an acid, a base, or a salt.

The method naturally divides itself into two cases: first, for the formation of insoluble salts; and second, for the formation of soluble salts.

86. The formation of insoluble salts. The method cannot be used intelligently at all, unless the student is familiar with the solubility of the various compounds involved. He should, therefore, either consult a solubility table, or, better, learn the following solubility rules, which will cover most of the common cases.

Solubility Rules

87. All of the hydrogen, sodium, potassium, and ammonium compounds are soluble; also all of the chlorates, acetates, and nitrates.

All of the chlorides are soluble, except those of silver, lead, and mercurous mercury.

All of the sulphates are soluble, except those of barium, stron-
tium, and lead.

All of the carbonates, phosphates, silicates, and sulphides are
insoluble, except those of sodium, potassium, and ammonium.

All of the hydroxides are insoluble, except those of sodium, potas-
sium, ammonium, calcium, strontium, and barium.

To make **barium sulphate,** which is insoluble, then, it is only necessary
to mix a solution of a soluble barium compound with a solution of a sul-
phate. Obviously, there are hundreds of reactions which would suffice:

$$BaCl_2 + H_2SO_4 = \underline{BaSO_4} + 2\,HCl.$$
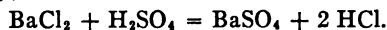
The equivalent number for the above equation was 2. Or we might
have mixed barium nitrate with aluminum sulphate. Barium having a
valence of 2 and aluminum having a valence of 3, the equivalent number
would be 6. So the equation would be:

$$3\,Ba(NO_3)_2 + Al_2(SO_4)_3 = 3\,\underline{BaSO_4} + 2\,Al(NO_3)_3.$$
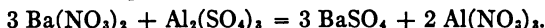
The method is especially adapted to the formation of insoluble com-
pounds, but it may also be used for the formation of soluble substances.

The formula of the insoluble compound should invariably have a line
drawn under it.

88. Exercise. Write equations showing the formation of
barium sulphate, silver chloride, and calcium phosphate, each
in ten different ways, making use of the above method.

89. The formation of soluble salts. In order to form soluble salts by
this method, it is necessary that the reagents be mixed in very exact pro-
portions, and also that some insoluble compound be formed at the same
time. It makes no difference what the nature of this insoluble substance
is, if the two reagents used are soluble.

Two or three insoluble compounds will usually suffice for the forma-
tion of almost any soluble salt. Silver chloride, barium sulphate, and
calcium carbonate are good ones to use.

It is plain that there must be four different kinds of radicals involved;
therefore it would be impossible to make a silver salt or a chloride when
silver chloride was the insoluble compound.

Again, one would not try to make a barium compound or a sulphate,
when barium sulphate was to be the insoluble substance.

Suppose it is desired to make potassium sulphate by this method and
that we expect to get silver chloride as a precipitate at the same time.
Then we must mix silver sulphate with potassium chloride. The numbers
involved are 1 and 2. The equation is

$$2\,KCl + Ag_2SO_4 = K_2SO_4 + 2\,\underline{AgCl}.$$
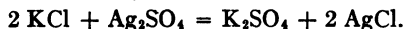
Again, suppose that we want to make sodium nitrate with calcium car-

bonate as the precipitate. Then we must use sodium carbonate and calcium nitrate. The number is again 2:

$$Ca(NO_3)_2 + Na_2CO_3 = 2\,NaNO_3 + CaCO_3.$$
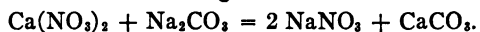
In the case of some soluble salts it will be found impossible to find two soluble compounds to use.

90. Exercise. Show by equations the formation of the same twenty-five salts by this method, indicating the cases which are practically impossible (77).

Sixth Method of Making Salts

·91. **The direct union of a basic with an acidic oxide.** All oxygen salts may be considered as made up of basic oxides united with acidic oxides. The method is put in here for the sole purpose of familiarizing the student with this fact. It is obviously applicable only to the formation of oxygen salts.

The equivalent number applies only to the basic metal. In general, it may be remembered that in the case of an acid-producing element having two valences, **it is the high oxide that gives rise to the salts whose names end in "ate," and the low oxide that forms salts with names ending in "ite."**

Thus, to show the formation of sodium sulphate, we should have to mix sodium oxide with the high oxide of sulphur, SO_3:

$$Na_2O + SO_3 = Na_2SO_4.$$
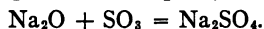
Calcium phosphate would be formed from calcium oxide and the high oxide of phosphorus, P_2O_5. The formula of the compound being $Ca_3(PO_4)_2$, we should have to use three molecules of calcium oxide:

$$3\,CaO + P_2O_5 = Ca_3(PO_4)_2.$$
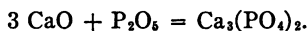
The quantity of the acidic oxide must be determined by inspection after the right quantity of the metal has been obtained.

If we wanted to make sodium arsenite we should have to use sodium oxide and arsenic trioxide. The formula of sodium arsenite, being Na_3AsO_3, contains three sodium atoms; and the formula of the oxide of sodium, containing two sodium atoms, calls for an equivalent number of 6. So we must use $3\,Na_2O$:

$$3\,Na_2O + As_2O_3 = 2\,Na_3AsO_3.$$

N_2O_5 forms two nitrate radicals, $2\,NO_3^{\cdot}$
P_2O_5 forms two phosphate radicals, $2\,PO_4^{\cdot\cdot\cdot}$
As_2O_3 forms two arsenite radicals, $2\,AsO_3^{\cdot\cdot\cdot}$
SO_3 forms one sulphate radical, $SO_4^{\cdot\cdot}$
CrO_3 forms one chromate radical, $CrO_4^{\cdot\cdot}$
SiO_2 forms one ortho-silicate radical, $SiO_4^{\cdot\cdot\cdot\cdot}$

92. Exercise. Write equations showing the formation of salts by combining each of the following oxides with each of the above acidic oxides:

$$Na_2O; K_2O; MgO; Al_2O_3; PbO; Fe_2O_3.$$
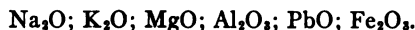
This kind of reaction is not common in the laboratory, as there are few solid acidic oxides available that can be used with effectiveness.

Sodium dioxide may, however, be mixed with the proper quantity of chromium trioxide in a small iron crucible with the instant formation of sodium chromate, and the mass extracted with water and crystallized in a few minutes.

Various basic oxides may be mixed with silica and fused to various colored glazes in a muffle-furnace.

SEVENTH METHOD OF MAKING SALTS

93. The action of an acid anhydride on a base. In this case water and a salt are formed. The action is essentially the same as the action of an acid on a base, for the acid anhydride acting on the water at once forms the corresponding acid. Or it might be considered the same as the action of a basic oxide on an acidic oxide, except that the water of the base is set free.

Thus, sodium hydroxide may be considered as made up of sodium oxide and water:

$$2\,NaOH = Na_2O + H_2O.$$

So, if we wished to make sodium carbonate, we should have to use sodium hydroxide and carbon dioxide. Examples:

$$2\,NaOH\,(Na_2O + H_2O) + CO_2 = Na_2CO_3 + H_2O.$$
$$\text{Or,} \qquad Ca(OH)_2 + SO_3 = CaSO_4 + H_2O;$$
$$2\,Al(OH)_3\,(Al_2O_3 + 3\,H_2O) + 3\,N_2O_5 = 2\,Al(NO_3)_3 + 3\,H_2O.$$
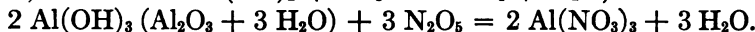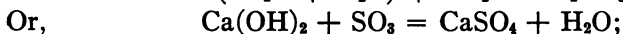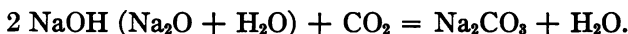
94. Exercise. Write equations showing the combination of each of the following acid anhydrides with each of the bases:

Acid anhydrides	Bases
CO_2	NH_4OH
SiO_2	$NaOH$
N_2O_5	KOH
SO_2	$Ca(OH)_2$
SO_3	$Ba(OH)_2$
CrO_3	$Sr(OH)_2$
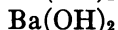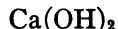
Questions

1. What is a reversible reaction? (72).   How may the direction of a reaction be changed? (73).
2. Name three conditions which result in completed reactions (74).
3. What is meant by solution pressure? (75).   What metals have high solution pressures? low pressures? (75).
4. State seven general methods for the preparation of salts (76–93).
5. Write equations showing the formation of any oxygen salt in seven different ways.
6. What is a stable and non-volatile acid? a stable and volatile acid? an unstable acid? (84).   Give examples of each kind.
7. State the complete solubility rule (87).   How should you prepare an insoluble salt? (87).
8. Any oxygen salt may be considered as being made up of what two compounds? (92).

CHAPTER VII

OXIDES OF THE ELEMENTS IN GROUPS IN RELATION TO ACIDS AND BASES (230)

95. Metals and non-metals. All the elements may be divided into two classes, **metals** and **non-metals**. In general, the oxides of the metals unite directly or indirectly with water to form bases. The oxides of the non-metals unite with water either directly or indirectly to form acids.

96. The first group. All the elements of this group are metals and form oxides of the general formula R_2O. Copper, in addition to cuprous oxide, Cu_2O, forms the oxide CuO, cupric oxide. These oxides are all base-producing:
$$Na_2O + H_2O = 2\,NaOH.$$

97. The second group. All the elements of this group are metals and form oxides of the general formula RO. Mercury, in addition to mercuric oxide, HgO, forms mercurous oxide, Hg_2O. These oxides are also all base-producing:
$$CaO + H_2O = Ca(OH)_2.$$
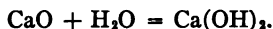
98. The third group. Two elements only are considered in this group, boron and aluminum. Aluminum forms the oxide Al_2O_3, which reacts with water indirectly to form the compound $Al(OH)_3$, which acts as a base toward strong acids and as an acid toward strong bases. Its formula as an acid might be written H_3AlO_3.

Boron is a non-metal and forms the oxide B_2O_3, which unites readily with water to form the compound $B(OH)_3$. This compound has only acid properties and is known as ortho-boric acid. Its formula is usually written H_3BO_3.

99. The fourth group. Carbon forms two oxides. The first, CO, forms neither acids nor bases. The second, CO_2, unites with water to form an unstable acid, $CO(OH)_2$, called carbonic acid, the formula for which is commonly written H_2CO_3.

Silicon forms one oxide, SiO_2, which forms a number of acids, when combined with varying amounts of water:
$$SiO_2 + H_2O = SiO(OH)_2, \text{ or } H_2SiO_3, \text{ meta-silicic acid.}$$
$$SiO_2 + 2\,H_2O = Si(OH)_4, \text{ or } H_4SiO_4, \text{ ortho-silicic acid.}$$
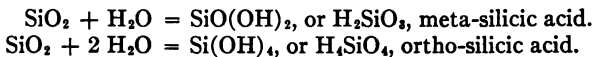
Tin forms two oxides, SnO, basic, and SnO_2, acidic:
$$SnO + H_2O = Sn(OH)_2.$$
$$SnO_2 + H_2O = SnO(OH)_2, \text{ or } H_2SnO_3, \text{ stannic acid.}$$
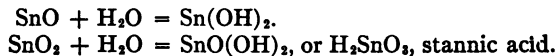
Lead forms several oxides, only one of which, PbO, need be considered. This oxide unites with water indirectly to form $Pb(OH)_2$, which is basic toward acids and weakly acidic toward bases.

100. The fifth group. Nitrogen forms several oxides, three of which are acid-producers:

$$N_2O + H_2O = 2\,HNO, \text{ hyponitrous acid.}$$
$$N_2O_3 + H_2O = 2\,HNO_2, \text{ nitrous acid.}$$
$$N_2O_5 + H_2O = 2\,HNO_3, \text{ nitric acid.}$$
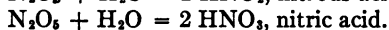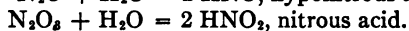
Phosphorus forms two oxides, each of which forms acids with water:

$$P_2O_3 + 3\,H_2O = 2\,P(OH)_3, \text{ or } 2\,H_3PO_3, \text{ phosphorous acid.}$$
$$P_2O_5 + H_2O = 2\,PO_2(OH), \text{ or } 2\,HPO_3, \text{ meta-phosphoric acid.}$$
$$P_2O_5 + 2\,H_2O = P_2O_3(OH)_4, \text{ or } H_4P_2O_7, \text{ pyrophoric acid.}$$
$$P_2O_5 + 3\,H_2O = 2\,PO(OH)_3, \text{ or } 2\,H_3PO_4, \text{ ortho-phosphoric acid.}$$
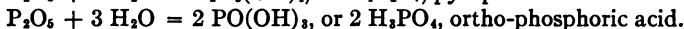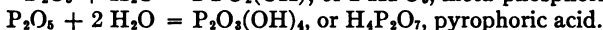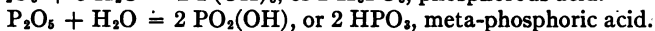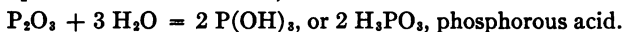
Arsenic and antimony form oxides and acids similar to those of phosphorus.

Bismuth forms the oxide Bi_2O_3, which forms bismuth hydroxide with water.

101. The sixth group. Sulphur forms two oxides, SO_2 and SO_3, both acidic:

$$SO_2 + H_2O = SO(OH)_2, \text{ or } H_2SO_3, \text{ sulphurous acid.}$$
$$SO_3 + H_2O = SO_2(OH)_2, \text{ or } H_2SO_4, \text{ sulphuric acid.}$$
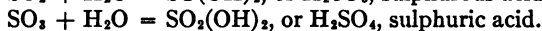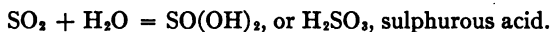
Chromium does not form the oxide CrO; but the corresponding hydroxide, $Cr(OH)_2$, is well known. Cr_2O_3, chromic oxide, is weakly basic, and forms chromic hydroxide, $Cr(OH)_3$. CrO_3, chromium trioxide, or chromic anhydride, is acidic and forms chromic acid:

$$CrO_3 + H_2O = CrO_2(OH)_2, \text{ or } H_2CrO_4, \text{ chromic acid.}$$
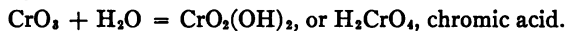
Two molecules of chromium trioxide may be considered as uniting with one molecule of water to form dichromic acid:

$$2\,CrO_3 + H_2O = Cr_2O_5(OH)_2, \text{ or } H_2Cr_2O_7.$$

102. The seventh group. This group, with the exception of manganese, may best be considered as forming a regular series of oxides and acids:

The only known oxides of chlorine are Cl_2O, ClO_2, and Cl_2O_7; yet the regular acids or the salts of these acids are known:

$$Cl_2O + H_2O = 2\,Cl(OH), \text{ or } 2\,HClO, \text{ hypochlorous acid.}$$
$$Cl_2O_3 + H_2O = 2\,ClO(OH), \text{ or } 2\,HClO_2, \text{ chlorous acid.}$$
$$Cl_2O_5 + H_2O = 2\,ClO_2(OH), \text{ or } 2\,HClO_3, \text{ chloric acid.}$$
$$Cl_2O_7 + H_2O = 2\,ClO_3(OH), \text{ or } 2\,HClO_4, \text{ per-chloric acid.}$$
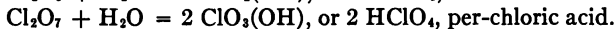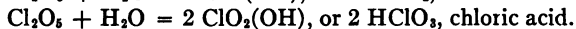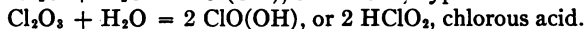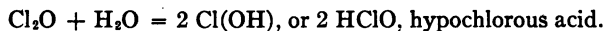
Bromine does not form any oxides; but the acids HBrO, hypobromous, and $HBrO_3$, bromic, are known.

Iodine may be considered as forming acids similar to the chlorine acids. Only one oxide has been prepared in the free condition, I_2O_5.

Manganese forms six oxides, some of which are basic and some acidic:

MnO, manganous oxide, basic, forming $Mn(OH)_2$.

Mn_2O_3, manganic oxide, basic, forming $Mn(OH)_3$.

MnO_2, manganese dioxide, acidic:

$$MnO_2 + H_2O = H_2MnO_3, \text{ manganous acid.} \quad \text{Not known free.}$$

MnO_3, manganic anhydride, acidic:

$$MnO_3 + H_2O = H_2MnO_4, \text{ manganic acid.}$$

Mn_3O_4, neither basic nor acidic.

Mn_2O_7, manganese heptoxide, or permanganic anhydride, acidic:

$$Mn_2O_7 + H_2O = 2\,HMnO_4, \text{ permanganic acid.}$$

103. The eighth group. The only elements considered in this group are iron, nickel, and cobalt. They form the regular oxides and hydroxides corresponding to the valences 2 and 3. Both the oxides and hydroxides are basic:

FeO, ferrous oxide, forms $Fe(OH)_2$, ferrous hydroxide.

Fe_2O_3, ferric oxide, forms $Fe(OH)_3$, ferric hydroxide.

NiO, nickelous oxide, forms $Ni(OH)_2$, nickelous hydroxide.

Ni_2O_3, nickelic oxide, forms $Ni(OH)_3$, nickelic hydroxide.

CoO, cobaltous oxide, forms $Co(OH)_2$, cobaltous hydroxide.

Co_2O_3, cobaltic oxide, forms $Co(OH)_3$, cobaltic hydroxide.

104. The system of naming acids and salts. The names of salts formed from "ous" acids end in "ite," and the names of salts formed from "ic" acids end in "ate."

If an acid has less oxygen than the usual "ous" acid, that is, if it represents a lower *stage of oxidation* (106), the prefix "hypo" is placed before the name of the "ous" acid. Thus, HNO_2 is nitrous acid, HNO is hyponitrous acid.

If an acid represents a higher stage of oxidation than the usual "ic" acid, the prefix "per" is placed before the name. Thus, $HClO_3$ is chloric acid and $HClO_4$ is perchloric acid.

105. The names and valences of radicals. The names of radicals are taken as the first or last part of the name of a salt. Thus:

$NaNO$ is sodium hyponitrite; NO is the hyponitrite radical and has a valence of 1 because it can form a compound with one hydrogen.

$Mg_2P_2O_7$ is magnesium pyrophosphate; P_2O_7 is the pyrophosphate radical and has a valence of 4 because it can exist in combination with four hydrogen atoms.

Questions

1. Name the oxides of the elements in groups and state whether they are base or acid forming (95–103).
2. Name several metals, the hydroxides of which act both as acids and bases (98, 99).
3. Is the hydroxide of an element necessarily basic? (98, 100).
4. If the name of an acid ends in "ous," what does the name of the salt end in? (104).
5. If the name of an acid ends in "ic," what does the name of the salt end in? (104).
6. Explain the use of the prefixes "hypo" and "per" in naming acids.

CHAPTER VIII

OXIDATION AND OXIDIZING AGENTS

106. Stage of oxidation. Most of the elements combine directly or indirectly with oxygen, forming oxides; and many of them combine with different quantities of oxygen, forming several different oxides. In such cases we must recognize what may be termed the **stage of oxidation.** An element may exist in its highest, lowest, or some intermediate stage of oxidation.

Let us consider the stages of oxidation of nitrogen. In the compound N_2O_5 we evidently have nitrogen in its highest stage of oxidation. In the compound N_2O_3 it is in a lower stage; and N_2 itself, in the free condition, is evidently in a lower stage than in N_2O_3. In the compound NH_3 the nitrogen must be in a still lower stage of oxidation; for the compound could evidently be treated with oxygen in such a way as to give free nitrogen.

Again, in the case of chlorine we must consider that the compound HCl contains the chlorine in a lower stage of oxidation than when it exists in the free condition. If hydrogen chloride be treated with oxygen, we get chlorine itself.

In general, we may consider an element combined with hydrogen alone to be in its lowest stage of oxidation.

107. Oxidation is the process of adding oxygen to or extracting hydrogen from a substance. It may also be considered as the process of changing an element from a lower to a higher stage of oxidation.

Thus, we have:

$$2\,Cu + O_2 = 2\,CuO;\ or$$
$$O_2 + 4\,HCl = 2\,H_2O + 2\,Cl_2.$$
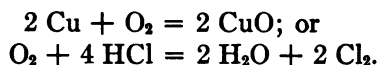
Chlorine is a product of the oxidation of hydrochloric acid. The direct addition of chlorine changes ferrous chloride to

ferric chloride, and it is proper to say that the ferrous chloride
is oxidized to ferric chloride by chlorine, thus:

$$2 \ FeCl_2 + Cl_2 = 2 \ FeCl_3.$$

108. An oxidizing agent is any substance that directly or in-
directly brings about oxidation. Any element in a high stage
of oxidation may be considered as an oxidizing agent.

109. Reduction is the process of extracting oxygen from or
adding hydrogen to a substance. Or it may be considered
as the process of changing an element from a higher to a lower
stage of oxidation.

110. A reducing agent is any substance that can directly or
indirectly bring about reduction. Almost any substance con-
taining an element in a low stage of oxidation may act as a re-
ducing agent.

All oxidizing processes may be divided into two classes,
oxidation in the "dry way" and oxidation in the "wet way."

OXIDATION IN THE "DRY WAY"

111. In cases of oxidation in the dry way the oxidizing
agent is commonly free gaseous oxygen or some substance that
readily gives up part or all of its oxygen. Such reactions take
place without the intervention of a liquid and either give
rise to or are brought about by high temperatures. All cases of
burning and combustion are examples of such oxidation (310).

Some Oxidizing Agents for the Dry Way

112. Oxygen.

Air.

$KClO_3$, potassium chlorate.

KNO_3, potassium nitrate.

Pb_3O_4, red lead.

MnO_2, manganese dioxide.

Many metallic oxides are oxidizing agents when heated with
some substance that combines very readily with oxygen.
Thus:

$$2 \ PbO + C = 2 \ Pb + CO_2.$$
$$2 \ Fe_2O_3 + 3 \ C = 4 \ Fe + 3 \ CO_2.$$
$$CuO + H_2 = Cu + H_2O.$$
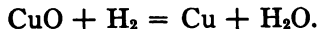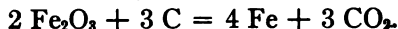
It should be noticed that in these cases the metallic oxide is the oxidizing agent and that the other substance is the reducing agent. Or, in other words, that the oxidizing agent oxidizes the reducing agent, and that the reducing agent reduces the oxidizing agent.

113. Exercise. Write equations showing the oxidation of each of the following reducing agents by each of the given oxidizing agents:

Reducing agents	Oxidizing agents
Hydrogen	Sodium oxide
Carbon	Magnesium oxide
Potassium	Aluminum oxide
Aluminum	Lead oxide
Magnesium	Tin dioxide
Carbon monoxide (CO)	Antimony trioxide
Methane (CH$_4$)	Manganese dioxide
Ethane (C$_2$H$_6$)	Nickelous oxide

OXIDATION IN THE WET WAY

114. Many oxidation reactions can best take place in a solution containing the oxidizing agent and the substance to be oxidized.

In such reactions no oxygen is actually set free in the gaseous form but enters at once into combination with the reducing agent. If there is an excess of the reducing agent, all of the oxidizing agent will be used up; and if there is an excess of the oxidizer, all of the reducing agent will be transformed.

The oxidizing agent may usually be dissolved alone without undergoing any change; but if the products of its possible decomposition may at once escape from the solution or enter a new chemical combination, the reaction will take place at once.

Oxidizing Agents for the Wet Way

115. As has already been said, a substance is an oxidizing agent if it contains an element in a high stage of oxidation when a lower stage is possible.

The elements which are capable of acting in this way are the ones whose oxides act as acid anhydrides and acidic oxides in the formation of acids and salts.

116. Nitric acid and nitrates. Nitrogen in its highest stage of oxidation forms the oxide N$_2$O$_5$. This with water forms nitric acid, and it may be considered as existing in all nitrates.

Nitric acid and all nitrates may therefore act as oxidizing agents.

Since there are several lower stages of oxidation of nitrogen, it may be

understood at once that nitric acid and nitrates might oxidize in several different ways, depending on the way they are used and the nature of the reducing agent. For the sake of uniformity it will be assumed that the nitrogen will always drop to the lower stage represented by the compound, nitric oxide, NO.

117. Oxidizing power. Oxidizing power may be considered as the number of atoms of oxygen that a given quantity of an oxidizing agent is capable of furnishing for oxidizing purposes.

When the low stage of oxidation of an acid-producing element has been decided upon, it is a simple matter to indicate the oxidizing power of one of its compounds.

OXIDIZING POWER OF TYPICAL OXIDIZERS

118. Nitrates. Nitrates, including nitric acid, all contain nitrogen in its highest stage of oxidation, N_2O_5. They may all be considered as breaking up, during oxidation, into water or a basic oxide, nitric oxide, and oxygen. Thus:

$$2 HNO_3 = H_2O + 2 NO + 3 O.$$
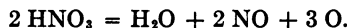
There will always be as many molecules of NO as there were of nitrate radicals:

$$2 KNO_3 = K_2O + 2 NO + 3 O.$$
$$2 Al(NO_3)_3 = Al_2O_3 + 6 NO + 9 O.$$
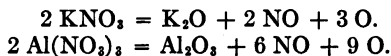
In the case of aluminum nitrate, it should be noticed that it is necessary to take two molecules in order to be able to indicate the formation of aluminum oxide. This makes six nitrate radicals on the left and necessitates six nitric oxide molecules on the right.

Two molecules of aluminum nitrate contain eighteen atoms of oxygen, nine of which are accounted for in the two oxides, leaving nine for oxidizing purposes (459).

119. Exercise. Write the formulas of the nitrates of all of the metals and determine the oxidizing power of each.

120. Manganates. Manganates, including manganic acid, all contain manganese in the stage of oxidation represented by the formula MnO_3.

Manganese in all compounds that act as oxidizers in the wet way may be considered to drop to the oxide MnO, manganous oxide, basic.

H_2MnO_4, manganic acid, would therefore break up as follows:

$$H_2MnO_4 = H_2O + MnO + 2 O.$$
$$K_2MnO_4 = K_2O + MnO + 2 O.$$
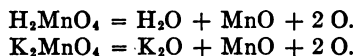
The manganate radical would have a valence of 2, and the formula for aluminum manganate would be $Al_2(MnO_4)_3$. It would oxidize as follows:

$$Al_2(MnO_4)_3 = Al_2O_3 + 3 MnO + 6 O.$$

121. Exercise. Write the formulas of the manganates of all of the metals, and indicate their oxidizing power.

122. Chromates. All chromates, including chromic acid, contain chromium in its highest stage of oxidation, CrO_3. The valence of chromium in this compound is 6. When it is involved in an oxidation reaction it usually drops to a valence of 3. The corresponding oxide is Cr_2O_3, chromic oxide, which is basic:

$$2 H_2CrO_4 = 2 H_2O + Cr_2O_3 + 3 O.$$

Here it was necessary to take two molecules in order to be able to indicate the formation of the oxide Cr_2O_3. There were eight oxygen atoms on the left; five were accounted for in the oxides on the right, and three were left for oxidizing purposes. The chromate radical is CrO_4, with a valence of 2. The formula for aluminum chromate would be $Al_2(CrO_4)_3$; it would oxidize as follows:

$$2 Al_2(CrO_4)_3 = 2 Al_2O_3 + 3 Cr_2O_3 + 9 O.$$

Here it was necessary to take two molecules in order to get an even number of chromium atoms (818).

123. Permanganates. Permanganates, including permanganic acid, all contain manganese in its highest stage of oxidation, represented by the formula Mn_2O_7.

During oxidation the manganese usually drops to its lowest stage, represented by the formula MnO.

The permanganate radical is MnO_4, with a valence of 1.

Permanganic acid, $HMnO_4$, would oxidize as follows:

$$2 HMnO_4 = H_2O + 2 MnO + 5 O.$$
$$2 KMnO_4 = K_2O + 2 MnO + 5 O.$$
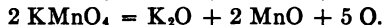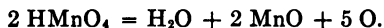
The formula of aluminum permanganate would be $Al(MnO_4)_3$. It would oxidize as follows:

$$2 Al(MnO_4)_3 = Al_2O_3 + 6 MnO + 15 O.$$

124. Exercise. Write the formulas of the permanganates of all of the metals, and indicate their oxidizing power.

125. Dichromates. The dichromates act exactly like the chromates, except that they contain twice as much chromium trioxide. The chromium trioxide, CrO_3, drops to chromic oxide, Cr_2O_3, which is basic.

The dichromate radical is Cr_2O_7, with a valence of 2. The formula for hydrogen dichromate, or dichromic acid, is $H_2Cr_2O_7$.

It would oxidize as follows:

$$H_2Cr_2O_7 = H_2O + Cr_2O_3 + 3 O.$$
$$K_2Cr_2O_7 = K_2O + Cr_2O_3 + 3 O.$$
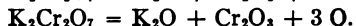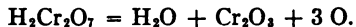
The formula of aluminum dichromate would be $Al_2(Cr_2O_7)_3$, and it would oxidize as follows:

$$Al_2(Cr_2O_7)_3 = Al_2O_3 + 3 Cr_2O_3 + 9 O.$$

126. Other oxidizing agents:

(a) Chlorine, in the presence of water, oxidizes as follows:

$$Cl_2 + H_2O = 2 HCl + O.$$
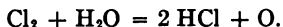
(b) Bromine, in the presence of water, oxidizes as follows:
$$Br_2 + H_2O = 2\ HBr + O.$$
(c) Iodine, in the presence of water, oxidizes as follows:
$$I_2 + H_2O = 2\ HI + O.$$
(d) Hydrogen peroxide decomposes readily into water and oxygen:
$$H_2O_2 = H_2O + O.$$
(e) Manganese dioxide:
$$MnO_2 = MnO + O.$$
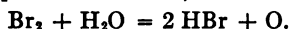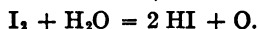
127. Summary of convenient oxidizers for use in the wet way:
1. $H_2O_2 = H_2O + O.$
2. $Cl_2 + H_2O = 2\ HCl + O.$
3. $Br_2 + H_2O = 2\ HBr + O.$
4. $I_2 + H_2O = 2\ HI + O.$
5. $2\ HNO_3 = H_2O + 2\ NO + 3\ O.$
6. $PbO_2 = PbO + O.$
7. $MnO_2 = MnO + O.$
8. $Pb_3O_4 = 3\ PbO + O.$
9. $K_2MnO_4 = K_2O + MnO + 2\ O.$
10. $K_2Cr_2O_7 = K_2O + Cr_2O_3 + 3\ O.$
11. $2\ KMnO_4 = K_2O + 2\ MnO + 5\ O.$
12. $2\ K_2CrO_4 = 2\ K_2O + Cr_2O_3 + 3\ O.$

Questions

1. What is meant by the stage of oxidation? Give a series of formulas indicating a variation in the stage of oxidation of some element (106).
2. What is oxidation? (107); an oxidizing agent? (108); reduction? (109); a reducing agent? (110).
3. Into what two classes may all oxidizing processes be divided? (110).
4. Name some oxidizing agents which might be used in the dry way (112).
5. Indicate by equations the reduction of various metallic oxides each by the use of sodium, carbon, carbon monoxide, and hydrogen.
6. How is it possible to estimate the oxidizing power of an oxidizing agent? (118).
7. Give the names of several classes of oxidizing agents and show how one example of each might oxidize (118–127).
8. Give the formulas of twelve common oxidizing agents and state how they oxidize (127).

CHAPTER IX

FORMATION OF EQUATIONS FOR OXIDATION REACTIONS IN THE WET WAY

128. The liberation of chlorine, bromine, and iodine from their hydrogen compounds. In order to set chlorine free from hydrochloric acid, it is only necessary to remove the hydrogen in the form of water. This may be accomplished with almost any oxidizing agent:

$$O + 2 HCl = H_2O + Cl_2.$$
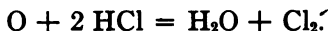
It is evident that there will always have to be twice as many molecules of the acid as there are available atoms of oxygen in the oxidizer. Also that the number of **molecules** of chlorine set free will always be the same as the number of available atoms of oxygen:

$$H_2O_2 = H_2O + O.$$
$$\underline{O + 2 HCl = H_2O + Cl_2.}$$
$$H_2O_2 + 2 HCl = 2 H_2O + Cl_2, \text{ final equation.}$$
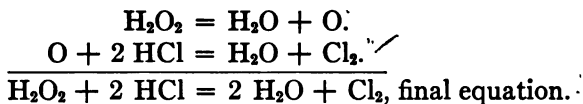
If the oxidizer is one that gives rise to basic oxides, these must be combined with an acid to form salts and water:

$$MnO_2 = MnO + O.$$
$$O + 2 HCl = H_2O + Cl_2.$$
$$\underline{MnO + 2 HCl = MnCl_2 + H_2O.}$$
$$MnO_2 + 4 HCl = MnCl_2 + 2 H_2O + Cl_2, \text{ final equation.}$$

$$2 KMnO_4 = K_2O + 2 MnO + 5 O.$$
$$5 O + 10 HCl = 5 H_2O + 5 Cl_2.$$
$$K_2O + 2 HCl = 2 KCl + H_2O.$$
$$\underline{2 MnO + 4 HCl = 2 H_2O + 2 MnCl_2.}$$
$$2 KMnO_4 + 16 HCl = 2 KCl + 2 MnCl_2 + 8 H_2O + 5 Cl_2.$$
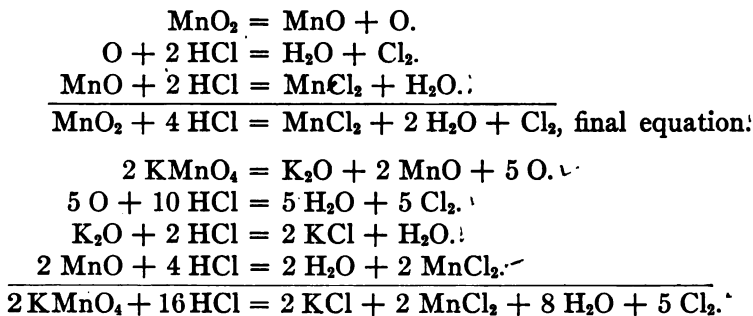
129. Exercise. Write equations showing the formation of chlorine, bromine, and iodine from their hydrogen compounds by the use of ten different oxidizing agents. It should be noted that, while at the start

it is desirable to write all of the partial equations before adding to get the final equation, it is not really necessary.

For example, suppose that it is desired to use potassium dichromate with hydrochloric acid:

$$K_2Cr_2O_7 = K_2O + Cr_2O_3 + 3 O.$$

The three atoms of O will require 6 HCl, two more will be necessary to unite with the K_2O, and six more for the Cr_2O_3, making 14 HCl altogether. Fourteen atoms of H will appear as 7 H_2O, and the three atoms of oxygen will give three molecules of chlorine.

The final equation will therefore be:

$$K_2Cr_2O_7 + 14 HCl = 2 KCl + 2 CrCl_3 + 7 H_2O + 3 Cl_2.$$
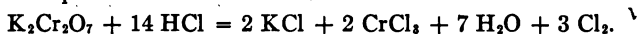
130. The liberation of chlorine, bromine, and iodine from their salts in the presence of sulphuric acid and an oxidizer. When a halogen salt is mixed with sulphuric acid and an oxidizer, the halogen is set free. It makes no difference in what order we assume the various reactions to take place. The partial equations are used simply as a means of working out the final equation.

Therefore, in this case, we may assume that the sulphuric acid acts on the salt and sets the halogen acid free; that the halogen acid is then oxidized with the formation of water and the halogen.

Finally, we may assume that all basic oxides are dissolved by sulphuric acid, forming sulphates.

It is a little easier to assume that the halogen salt is oxidized directly with the formation of a metallic oxide and the liberation of the halogen; then, that all basic oxides are changed to sulphates by the action of sulphuric acid. For example:

$$MnO_2 = MnO + O.$$
$$O + 2 NaCl = Na_2O + Cl_2.$$
$$MnO + H_2SO_4 = MnSO_4 + H_2O.$$
$$Na_2O + H_2SO_4 = Na_2SO_4 + H_2O.$$

$$MnO_2 + 2NaCl + 2H_2SO_4 = MnSO_4 + Na_2SO_4 + 2H_2O + Cl_2.$$
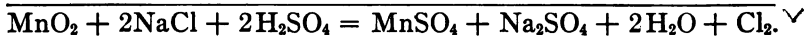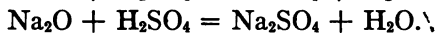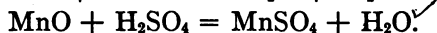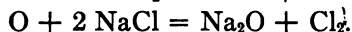
Here, again, it is not necessary actually to write all of the partial equations. Suppose that we wanted to use potassium permanganate with sodium chloride and sulphuric acid, to show the formation of chlorine. It is really only necessary to know the oxidizing power:

$$2 KMnO_4 = K_2O + 2 MnO + 5 O.$$
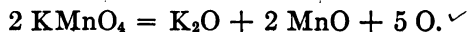
Five atoms of O are equivalent to 5 Cl_2, to 10 NaCl, and to 5 H_2SO_4. One more sulphuric acid molecule is necessary for the K_2O and two more for the 2 MnO, making 8 H_2SO_4 necessary altogether. In this case there will be as many molecules of water as there are molecules of acid.

The final equation would therefore be:

$$2\ KMnO_4 + 10\ NaCl + 8\ H_2SO_4 = K_2SO_4 + 2\ MnSO_4 + 8\ H_2O$$
$$+\ 5\ Cl_2 + 5\ Na_2SO_4.$$
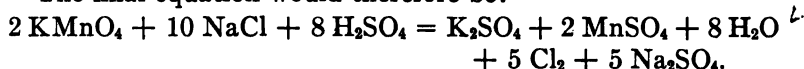
131. Exercise. Write equations showing the formation of the halogens from halogen salts in the presence of each of ten oxidizing agents and sulphuric acid.

132. The oxidation of non-metals. (*a*) In case it is desired to oxidize a non-metal to an oxygen acid, it is first oxidized to the corresponding acid anhydride, and the latter treated with the requisite quantity of water.

Sulphur to sulphuric acid by means of nitric acid:

$$2\ HNO_3 = H_2O + 2\ NO + 3\ O.$$
$$3\ O + S = SO_3.$$
$$\underline{SO_3 + H_2O = H_2SO_4.}$$
$$2\ HNO_3 + S = H_2SO_4 + 2\ NO.$$
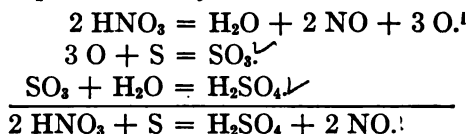
The NO is a gas which passes off in the air.

(*b*) If it is simply desired to oxidize sulphur to the sulphate condition, almost any oxidizing agent will suffice, provided there is sulphuric acid enough present to combine with any possible basic oxides.

Sulphur to the sulphate condition by means of potassium dichromate:

$$K_2Cr_2O_7 = K_2O + Cr_2O_3 + 3\ O.$$
$$3\ O + S = SO_3.$$
$$SO_3 + H_2O = H_2SO_4.$$
$$K_2O + H_2SO_4 = K_2SO_4 + H_2O.$$
$$\underline{Cr_2O_3 + 3\ H_2SO_4 = Cr_2(SO_4)_3 + 3\ H_2O.}$$
$$K_2Cr_2O_7 + S + 3\ H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3\ H_2O.$$
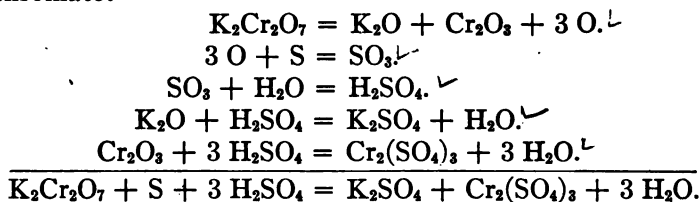
After a little practice it will not be necessary to write all of the partial equations. In the above case, three atoms of O are available. These are equivalent to one of sulphur, which requires one molecule of water and forms one molecule of sul-

phuric acid. Four molecules of H_2SO_4 are necessary to dis-
solve the basic oxides; therefore only three will be required.
These three will form three molecules of water.

133. **Oxidation of hydrogen sulphide to sulphuric acid.** In order
to bring about this oxidation, it is evidently necessary to add
four oxygen atoms to the H_2S.

Two molecules of nitric acid furnish only three atoms of
oxygen for oxidizing purposes. In order that the quantity of
oxygen furnished by the oxidizer shall be exactly sufficient, it
is necessary to use eight molecules of nitric acid, which will give
exactly twelve atoms of oxygen, sufficient exactly to oxidize
three molecules of H_2S. The equations then become:

$$8\ HNO_3 = 4\ H_2O + 8\ NO + 12\ O.$$
$$\underline{3\ H_2S + 12\ O = 3\ H_2SO_4.}$$
$$8\ HNO_3 + 3\ H_2S = 3\ H_2SO_4 + 8\ NO + 4\ H_2O.$$
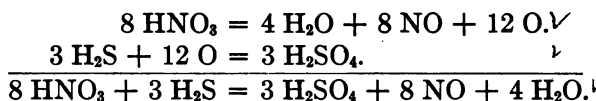
In the case of oxidizing agents containing basic oxides, they
should be combined with sulphuric acid, and it may happen that
all of the sulphuric acid formed will cancel out; nevertheless
the sulphur will remain in the sulphate condition.

134. **Exercise.** Write equations showing the oxidation of
hydrogen sulphide to the sulphate condition, by the use of ten
different oxidizing agents in the presence of sulphuric acid.

135. **Phosphorus to phosphoric acid, or to the phosphate condi-
tion.** The stage of oxidation of phosphorus in phosphates is
represented by the formula P_2O_5. Each 2 atoms of phos-
phorus must therefore have 5 atoms of oxygen. It will be
necessary to have enough of the oxidizing agent to give some
multiple of 5 atoms of oxygen:

$$2\ HNO_3 = H_2O + 2\ NO + 3\ O.$$
$$2\ P + 5\ O = P_2O_5.$$
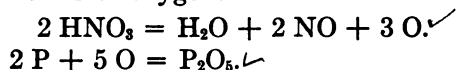
Here it is apparent that the oxygen is furnished in multiples
of 3, and it is needed in multiples of 5. It is therefore neces-
sary to use 15. Multiplying the first equation by 5 and the
second by 3 gives:

$$10\ HNO_3 = 5\ H_2O + 10\ NO + 15\ O.$$
$$6\ P + 15\ O = 3\ P_2O_5.$$
$$\underline{3\ P_2O_5 + 9\ H_2O = 6\ H_3PO_4.}$$
$$10\ HNO_3 + 6\ P + 4\ H_2O = 6\ H_3PO_4 + 10\ NO.$$
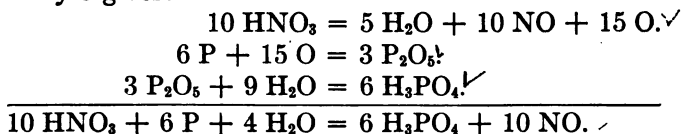
If oxidizing agents containing basic oxides are used, for the sake of uniformity the basic oxides should be changed to sulphates by the addition of a sufficient quantity of sulphuric acid.

136. Arsenic trioxide to arsenic acid. The trioxide must have two oxygen atoms added to it in order to raise it to the pentoxide. If the oxidizing agent used furnishes oxygen in multiples of 3, it will be necessary to use six oxygens:

$$3 \, As_2O_3 + 6 \, O = 3 \, As_2O_5.$$
$$4 \, K_2CrO_4 = 4 \, K_2O + 2 \, Cr_2O_3 + 6 \, O.$$
$$3 \, As_2O_5 + 9 \, H_2O = 6 \, H_3AsO_4.$$
$$4 \, K_2O + 4 \, H_2SO_4 = 4 \, K_2SO_4 + 4 \, H_2O.$$
$$2 \, Cr_2O_3 + 6 \, H_2SO_4 = 2 \, Cr_2(SO_4)_3 + 6 \, H_2O.$$
$$\overline{3 \, As_2O_3 + 4 \, K_2CrO_4 + 10 \, H_2SO_4 = 6 \, H_3AsO_4 + 4 \, K_2SO_4 +}$$
$$2 \, Cr_2(SO_4)_3 + H_2O.$$
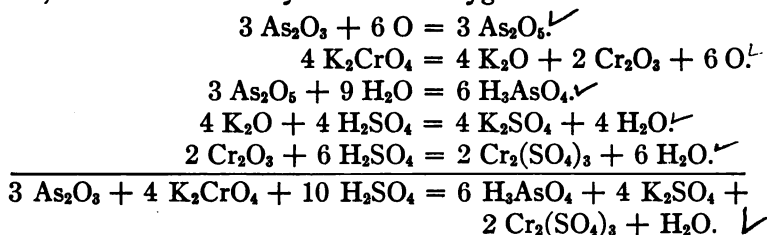
137. Exercise. Write equations showing the oxidation of phosphorus and arsenic to the corresponding oxygen acids, by the use of ten different oxidizing agents in the presence of sulphuric acid.

138. Oxidation by means of sulphuric acid. Boiling concentrated sulphuric acid is an oxidizing agent according to the equation:

$$H_2SO_4 = H_2O + SO_2 + O.$$

Many metals are oxidized by it with the formation of the sulphate, water, and sulphur dioxide. The reaction suffices for the preparation of the latter gas (404):

$$H_2SO_4 = H_2O + SO_2 + O.$$
$$O + Cu = CuO.$$
$$\underline{CuO + H_2SO_4 = CuSO_4 + H_2O.}$$
$$Cu + 2 \, H_2SO_4 = CuSO_4 + 2 \, H_2O + SO_2.$$
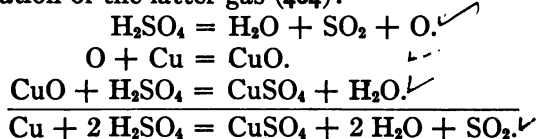
139. Exercise. Indicate the production of sulphur dioxide by the action of concentrated sulphuric acid on ten different metals, also on carbon and sulphur.

140. The action of nitric acid on metals. As has already been stated, nitric acid may oxidize in several different ways, depending on the concentration of the acid, the temperature, and the metal. In many cases, however, nitric oxide is formed, and

in the following work it will be assumed that it is always formed.

The oxygen from the acid unites with the metal and forms the oxide, which dissolves at once in more of the acid to form the nitrate of the metal:

$$2 \text{ HNO}_3 = \text{H}_2\text{O} + 2 \text{ NO} + 3 \text{ O}.$$
$$3 \text{ O} + 3 \text{ Cu} = 3 \text{ CuO}.$$
$$3 \text{ CuO} + 6 \text{ HNO}_3 = 3 \text{ Cu(NO}_3)_2 + 3 \text{ H}_2\text{O}.$$
$$\overline{3 \text{ Cu} + 8 \text{ HNO}_3 = 3 \text{ Cu(NO}_3)_2 + 4 \text{ H}_2\text{O} + 2 \text{ NO}.}$$
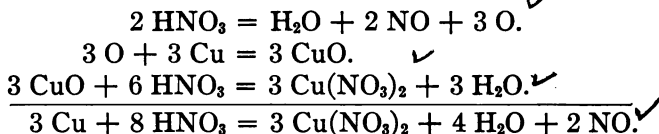
141. Exercise. Indicate the formation of nitric oxide by the action of nitric acid on ten different metals.

142. The complete oxidation of compounds of carbon and hydrogen. When a compound of carbon and hydrogen burns, the carbon changes to carbon dioxide and the hydrogen to water. If the compound contained nitrogen, the nitrogen is usually set free unchanged:

$$\text{CH}_4 + 2 \text{ O}_2 = \text{CO}_2 + 2 \text{ H}_2\text{O}.$$
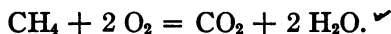
The oxygen can of course be furnished by any kind of an oxidizing agent. It is necessary to find, first, how much oxygen is required and then take enough of the oxidizing agent to furnish the required quantity. The formula for alcohol is $\text{C}_2\text{H}_6\text{O}$. The two atoms of carbon will require four atoms of oxygen and the six atoms of hydrogen will require three atoms of oxygen, making seven atoms altogether. But the molecule of alcohol already has one atom of oxygen in it. Therefore only six will be required:

$$4 \text{ HNO}_3 = 2 \text{ H}_2\text{O} + 4 \text{ NO} + 6 \text{ O}.$$
$$\underline{\text{C}_2\text{H}_6\text{O} + 6 \text{ O} = 2 \text{ CO}_2 + 3 \text{ H}_2\text{O}.}$$
$$4 \text{ HNO}_3 + \text{C}_2\text{H}_6\text{O} = 2 \text{ CO}_2 + 5 \text{ H}_2\text{O} + 4 \text{ NO}.$$
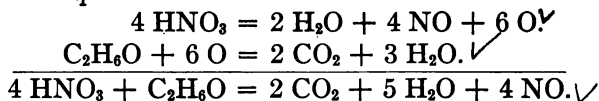
If the compound contains an odd number of atoms of hydrogen, it will be necessary to take double the quantity in order to have an even number.

143. Oxidation reactions involving a change of the basic radical from lower to higher valence. Suppose that it is desired to change cuprous chloride, CuCl, to cupric chloride, CuCl_2.

This may be accomplished by the direct addition of chlorine.

It may also be accomplished by the addition of hydrochloric acid and an oxidizer. The oxidizer will remove the hydrogen

from the hydrochloric acid and then the chlorine will add itself directly to the cuprous chloride:

$$2\ HNO_3 = H_2O + 2\ NO + 3\ O.$$
$$3\ O + 6\ HCl = 3\ H_2O + 6\ Cl.$$
$$6\ CuCl + 6\ Cl = 6\ CuCl_2.$$
$$\overline{6\ CuCl + 2\ HNO_3 + 6\ HCl = 6\ CuCl_2 + 4\ H_2O + 2\ NO.}$$
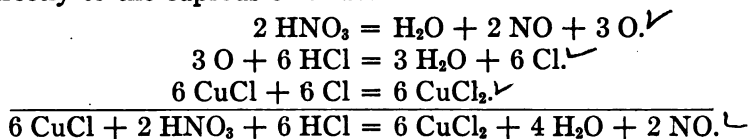
Here, since the smallest quantity of oxygen furnished was three atoms, the smallest quantity of chlorine possible was six atoms, which is just sufficient to change six molecules of cuprous chloride to cupric.

144. To change ferrous sulphate to ferric sulphate. The formula for ferrous sulphate is $FeSO_4$, and for ferric sulphate $Fe_2(SO_4)_3$. It is evident, then, that two ferrous sulphate molecules will be necessary to form one ferric sulphate molecule; also, that one additional sulphate radical will be necessary:

$$2\ KMnO_4 = K_2O + 2\ MnO + 5\ O.$$
$$5\ O + 5\ H_2SO_4 = 5\ H_2O + 5\ SO_4.$$
$$10\ FeSO_4 + 5\ SO_4 = 5\ Fe_2(SO_4)_3.$$
$$K_2O + H_2SO_4 = K_2SO_4 + H_2O.$$
$$2\ MnO + 2\ H_2SO_4 = 2\ MnSO_4 + 2\ H_2O.$$
$$\overline{10\ FeSO_4 + 8\ H_2SO_4 + 2\ KMnO_4 = 5\ Fe_2(SO_4)_3 + K_2SO_4 +}$$
$$2\ MnSO_4 + 8\ H_2O.$$
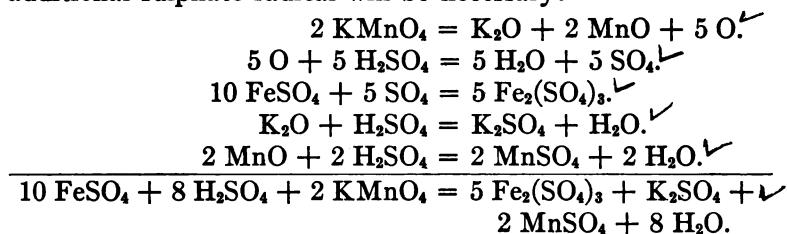
In this case the smallest quantity of oxygen that could be used was five atoms. These would be equivalent to five sulphate radicals; and, as two molecules of ferrous sulphate were required for each additional sulphate radical, ten ferrous sulphate molecules were needed.

145. The oxidation of ferrous chloride to ferric sulphate. It would take two ferrous chloride molecules to furnish iron enough for one ferric sulphate molecule, and four chlorine atoms would have to be set free.

In place of the four chlorine atoms three sulphate radicals must be added:

$$2\ HNO_3 = H_2O + 2\ NO + 3\ O.$$
$$3\ O + 3\ H_2SO_4 = 3\ H_2O + 3\ SO_4.$$
$$2\ FeCl_2 + 3\ SO_4 = Fe_2(SO_4)_3 + 2\ Cl_2.$$
$$\overline{2\ FeCl_2 + 2\ HNO_3 + 3\ H_2SO_4 = Fe_2(SO_4)_3 + 2\ NO +}$$
$$4\ H_2O + 2\ Cl_2.$$
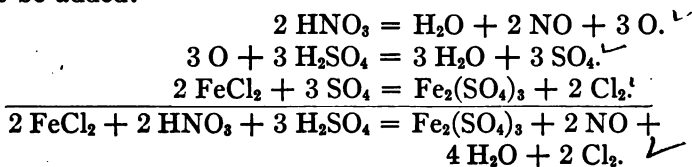
It should be noted that, although free radicals are indicated in the partial equations, they do not appear in the final equation, and that they are used as a convenient means of arriving at the final result.

146. Exercise. Indicate by equations the following oxidations, making use in each case of any oxidizing agent. Where basic oxides are concerned enough sulphuric acid should be used to change them to the corresponding sulphates and water:

1. C to CO_2.
2. H to H_2O.
3. CH_4, methane, to $CO_2 + H_2O$ (142).
4. C_2H_5OH, alcohol, to $CO_2 + H_2O$ (142).
5. C_2H_5OH to CH_3CHO, aldehyde (142).
6. C_2H_5OH to CH_3COOH, acetic acid.
7. S to SO_2.
8. S to SO_3 (132 a).
9. H_2S to $H_2O + S$.
10. H_2S to H_2SO_4 (133).
11. HCl to $H_2O + Cl$ (128).
12. HBr to $H_2O + Br$ (128).
13. HI to $H_2O + I$ (128).
14. HI to HIO_3, iodic acid.
15. $H_2C_2O_4$, oxalic acid, to $H_2O + CO_2$ (142).
16. $C_{17}H_{35}CO_2H$, stearic acid, to $H_2O + CO_2$ (142).
17. $FeCl_2$ to $FeCl_3$ (143).
18. $SnCl_2$, stannous chloride, to $SnCl_4$, stannic chloride (143).
19. HgCl to $HgCl_2$ (143).
20. $FeSO_4$, ferrous sulphate, to $Fe_2(SO_4)_3$, ferric sulphate (144).
21. P to H_3PO_4, ortho-phosphoric acid (135).
22. P_2O_3 to H_3PO_4 (136).
23. As to H_3AsO_4, arsenic acid.
24. As_2O_3 to H_3AsO_4 (136).

CHAPTER X

REDUCTION REACTIONS

147. Reduction is the process of changing an element from a higher to a lower stage of oxidation. It is exactly the opposite of oxidation.

148. Reducing agent. Any substance that can bring about reduction is a reducing agent.

Reduction is almost always accompanied by oxidation. The reducing agent reduces some substance which may be considered as an oxidizing agent. Whether the reaction is considered as a case of oxidation or reduction is simply a question of which process will bring about the required result.

149. Reduction in the " dry way." Reduction reactions in the dry way usually take place at high temperatures and are especially available for the reduction of metallic oxides to the corresponding metals. Some of these have already been referred to under the head of oxidation in the dry way.

Reducing Agents for the Dry Way

Any substance that burns with great energy in the air may be considered as a good reducing agent. Some of such reagents are: H, C, CH_4 (methane), CO, Na, K, Mg, Al, Fe, Si, and Ca.

150. Exercise. Indicate the reduction of all of the metallic oxides with each of the above reducing agents:

$$Fe_2O_3 + 3 H_2 = 2 Fe + 3 H_2O. \text{ } ✓$$
$$4 Cu_2O + CH_4 = 8 Cu + CO_2 + 2 H_2O. \text{ } ✓$$
$$Cr_2O_3 + 2 Al = 2 Cr + Al_2O_3. \text{ } ✓$$
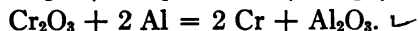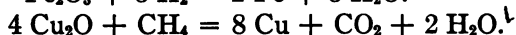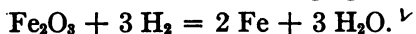
151. Reduction in the "wet way." Reduction in the wet way usually takes place in solution and therefore at comparatively low temperatures.

Reducing Agents for the Wet Way

Metals that dissolve readily in acids with the liberation of hydrogen, salts containing metals in a low stage of oxidation,

and unstable compounds of hydrogen form good reducing agents. Some of such reagents are:

Na, Mg, Al, $FeSO_4$, $FeCl_2$, $SnCl_2$, H_2SO_3, H_2S, and HI.

152. Exercise. Indicate by equations the following reductions:

1. $CuCl_2$ to CuCl with copper.
2. $HgCl_2$ to HgCl with mercury.
3. $HgCl_2$ to HgCl with $SnCl_2$.
4. $FeCl_3$ to $FeCl_2$ with H_2S, $SnCl_2$, or H_2SO_3.
5. $Fe_2(SO_4)_3$ to $FeSO_4$ with Fe or H_2S.
6. HNO_3 to NH_3 with H.
7. HNO_3 to NH_3 with Zn.
8. H_2SO_4 to H_2SO_3 with Cu or C.

153. Chemical equivalence between compounds. In general, the quantities of substances represented in any complete equation are chemically equivalent for that particular reaction.

In reactions where there is no change of valence, two substances are chemically equivalent when there are enough molecules of each to give the same total valence of either the basic or acid radicals. Thus:

H_3PO_4 is equivalent to three molecules of HCl, HNO_3, or NaOH.

$2 H_3PO_4$ is equivalent to $3 H_2SO_4$, $3 CaCl_2$, or $3 Ba(OH)_2$.

H_2SO_4 is equivalent to 2 HCl, $2 HNO_3$, 2 NaCl, or 2 NaOH.

In the case of a reaction involving a change of valence, the equivalence between any two compounds concerned is best obtained by writing the complete equation for the reaction; thus, in the case of the oxidation of ferrous sulphate with potassium permanganate, we have:

$$10 FeSO_4 + 8 H_2SO_4 + 2 KMnO_4 = Fe_2(SO_4)_3 + K_2SO_4 + 2 MnSO_4 + 8 H_2O.$$
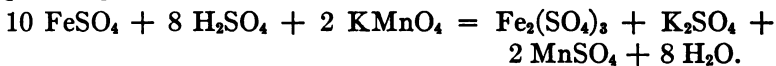
$KMnO_4$ is exactly equivalent to 5 $FeSO_4$, or to 5 Fe.

A certain quantity of one substance is said to be chemically equivalent to a definite quantity of another substance, when they can both be completely involved in the same reaction, or can each react with a fixed quantity of another substance.

Questions

1. What is reduction? (148); a reducing agent? Give examples of reducing agents for use in the dry way (149).
2. Indicate by equations the reduction of the metallic oxides to the metals by the use of ten different reducing agents (150).
3. When are two substances said to be chemically equivalent? (153).
4. 10 g. of ferrous sulphate would be equivalent to how many grams of potassium permanganate? (153, 252).
5. 10 g. of ferrous chloride would be equivalent to how many grams of ferric chloride? (153, 252).
6. How could you change ferric sulphate to ferrous sulphate? (152).

PART III

MORE ADVANCED THEORY

CHAPTER XI

THE NATURE OF GASEOUS BODIES

154. Motion of gas molecules. All gaseous bodies, that is, gases and vapors, are supposed to be made up of an almost infinite number of molecules travelling in straight lines with enormous velocity. Their directions are constantly altered by interference with each other or with the walls of the enclosing vessel, but they are always deflected in straight lines. The path of a single molecule is therefore made up of a continuous broken line, the straight portions of which are very long compared with the size of the molecules. **The velocity of gaseous molecules of a given kind depends** on the temperature alone. If the temperature be raised, the molecular velocity is increased.

The relative velocity of gaseous molecules can be determined by measuring the relative rates at which different gases escape through very small openings in very thin walls. From this it appears that the velocities are to each other **inversely as the square roots of the gas densities** (220).

Gaseous pressure is due to the multitude of impacts of the molecules against the walls of the enclosing vessel.

155. Boyle's law. At constant temperature the volume of a gas varies inversely as the pressure. That is, if the volume be reduced to one-half of what it was, the pressure will be doubled.

This corresponds exactly with the above theory, for if the volume be decreased to one-half of what it was, there will be twice as many molecules per unit of volume and consequently twice as many striking the walls and producing pressure as there were before.

This law may be more generally expressed by the equation,

$$\frac{P}{P'} = \frac{V'}{V}, \text{ or } PV = P'V',$$

in which P and P' are the two different pressures to which a body of gas is subjected at constant temperature, and V and V' are the corresponding volumes.

156. Effect of temperature. If a volume of gas at 0° C. be heated sufficiently to increase its temperature 1°, its volume will be increased $\frac{1}{273}$ of what it was at 0° C. And for each additional change of 1° the volume will change $\frac{1}{273}$ of what it was at 0° C. Therefore, if the temperature of a volume of gas at 0° C. be decreased 273°, the volume will theoretically become zero.

This temperature, 273° below zero, is known as **absolute zero.** Temperatures reckoned from this point are known as **absolute temperatures.** Common temperatures are changed to absolute temperatures by adding 273.

157. The law of Charles. At a constant pressure the volume of a body of gas varies directly as its absolute temperature.

This law may be more generally expressed by the equation,

$$\frac{V}{V'} = \frac{T}{T'}, \text{ or } VT' = V'T,$$

in which V and V' are the volumes of a body of gas at constant pressure, corresponding to the absolute temperatures T and T'.

158. Given the volume of a body of gas at known temperature and pressure, to compute the corresponding volume, temperature, or pressure under other known conditions.

Let V be the given volume at the temperature T and pressure P. Assuming that the temperature remains constant, let V' be the new volume corresponding to the new pressure P°. Then we have:

$$PV = P°V', \text{ or } V' = \frac{PV}{P°}.$$

Now let us assume that the pressure remains constant and that the temperature be allowed to become T°. The gas will

assume a new volume, which we shall call V°. Applying the law of Charles, we have $V'T^\circ = V^\circ T$; substituting the value of V' from above, we have:

$$\frac{PV}{P^\circ} T^\circ = V^\circ T, \text{ or } \frac{PV}{T} = \frac{P^\circ V^\circ}{T^\circ}.$$

This is the general gas law. P, V, and T will always be known, also two of the other factors, making it a very simple matter to determine the remaining one.

159. **Example.** The volume of a body of gas is measured at a temperature of 22° and a pressure of 780 mm., and found to be 25 c.c.; what would be the corresponding volume at a temperature of 100° and a pressure of 1000 mm.? Substituting in the above formula, we have:

$$\frac{25 \times 780}{295} = V^\circ \frac{1000}{373}, \text{ or } V^\circ = \frac{25 \times 780 \times 373}{295 \times 1000}.$$

NOTE. Since the volumes of gases are always measured subject to atmospheric pressure, it is customary to speak of the pressures as millimeters of mercury, the actual pressure being due to the weight of a column of mercury a certain number of millimeters high.

160. **Normal temperature and pressure.** Measured volumes of gases are generally reduced to the corresponding volume at 0° C. and 760 mm. pressure, known as **normal temperature and pressure:**

$$\frac{PV}{T} = \frac{P^\circ V^\circ}{T^\circ} = \frac{760}{273} V^\circ;$$

$$V^\circ = \frac{273}{760} \times \frac{P}{t + 273} V = .35921 \frac{PV}{273 + t},$$

in which V° is the required volume and t the observed temperature, and P the actual pressure to which the gas is subjected at the time the volume V is read. It is equal to the barometric pressure minus the vapor pressure of the liquid in contact with the gas, at the temperature t.

161. **Exercise.** 1. Change any given volume of a gas from any given temperature and pressure to the corresponding volume at any other temperature and pressure.

2. Compute the temperature or the pressure of a volume of a body of gas at known pressure and temperature corresponding to a required volume and temperature or volume and pressure.

3. Reduce a given volume of gas from known temperature and pressure to normal temperature and pressure.

EVAPORATION AND CONDENSATION

162. Evaporation and the nature of a vapor. At a constant temperature, a liquid in an enclosed space evaporates until the number of molecules escaping per unit of time is equalled by the number of gaseous molecules re-entering the liquid condition. A definite condition of equilibrium is then established.

The rate of evaporation increases with increase of temperature and decrease of pressure. The presence of substances dissolved in the liquid not only decreases the tendency for vapor to form, but may cause the vapor to condense to the liquid form.

A vapor that is in equilibrium with its liquid is said to be **saturated.** If the pressure due to a saturated vapor in contact with its liquid be suddenly reduced, vapor will form in the liquid at other points than on the surface, and the liquid is said to boil.

Water evaporating at the sea-level in contact with the atmosphere is constantly subject to a pressure of about fifteen pounds to the square inch. If the temperature be increased the vapor pressure will finally become great enough to lift the atmosphere away from the surface and the liquid will boil. The **boiling-point** is the temperature at which the vapor pressure equals the atmospheric pressure. Water boils at low temperatures on high mountains, and will boil at ordinary temperatures in a vacuum.

A saturated vapor at a given temperature has a definite number of molecules per unit volume. These travel in straight lines like the molecules of a gas and exert pressure on the walls of the enclosing vessel. If the volume be decreased at constant temperature, some of the vapor enters the liquid condition, and the number of molecules per unit volume remains unchanged. In other words, the volume of a saturated vapor may be decreased without an increase of pressure.

163. **Condensation and liquefaction.** A liquid in an enclosed space at a given temperature is always in contact with its saturated vapor. This vapor exerts a definite pressure, which is dependent on the temperature alone.

If the pressure be kept constant and the temperature reduced, the vapor will constantly change to the liquid form, or condense. If the temperature be maintained constant and the pressure increased, condensation will again take place.

164. **Critical temperature and pressure.** If a liquid be contained in an enclosed space in contact with its saturated vapor and the temperature be increased, the liquid will evaporate, and the pressure of the vapor will increase. This will continue until the density of the vapor is the same as that of the liquid; and the surface of the liquid, that is, the line of demarcation between the vapor and liquid, will disappear, the two becoming identical. The temperature at which this takes place is known as the **critical temperature.** In other words, **the critical temperature is that above which no amount of compression will cause the gas to condense. Critical pressure is the pressure just sufficient to cause a vapor to condense at its critical temperature.**

Questions

1. What is the nature of the motion of a gaseous molecule? To what is gaseous pressure due? How do the velocities of gas molecules vary with the molecular weight? (**154**).
2. How does the volume of a body of gas vary with the pressure? (**155**).
3. How does the volume of a body of gas vary with the temperature? (**156**).
4. What is absolute zero? absolute temperature? How is ordinary temperature converted to absolute? (**156**).
5. State both Boyle's and Charles's laws (**157**).
6. The volume of a body of gas measured at 30° and 800 mm. is found to be 100 c.c.; what would be the volume at normal temperature and pressure? (**158**).
7. State the general gas law (**158**).
8. What is meant by normal temperature and pressure? (**160**).
9. Does a vapor obey Boyle's law? (**162**).
10. Define the terms critical temperature and pressure (**164**).

CHAPTER XII

SOLUTION AND CRYSTALLIZATION

165. Tendency to establish equilibrium. In all natural changes in matter, both physical and chemical, that are constantly taking place on the earth, the change is invariably in such a direction that a more stable system of matter results. That is, in a direction which tends to produce a condition of equilibrium between the two kinds or states of matter.

If equilibrium is possible between the two kinds or states of matter concerned, the change will continue until it is established; and both kinds or states of matter will exist in the final system. If equilibrium is impossible, the action will continue until one of the kinds or states of matter has disappeared.

In the case of a liquid in an enclosed vessel at a constant temperature, the liquid will evaporate until the number of molecules escaping into the gaseous form is exactly balanced by the number re-entering the liquid condition. The space above the liquid is then said to be saturated with the vapor of the liquid.

If the vessel was not covered, some of the vapor would escape and the liquid would continue to evaporate until it was all gone, for it would be impossible to reach the condition of equilibrium.

166. Solution. When a soluble substance, called a **solute**, is placed in a liquid, molecules of the substance enter the dissolved condition.

This process continues until the number of molecules entering the liquid per unit of time is just equalled by the number of molecules re-entering the original form of the solute. A condition of equilibrium is then established, provided there was not enough of the liquid to dissolve all of the solute.

The liquid in which a solute is dissolved is called the **solvent**. Solutions are usually transparent. Finely divided solid or liquid particles uniformly distributed through a liquid render

it opaque, or non-transparent. Such mixtures are called suspensions and should not be confused with solutions.

Many substances apparently dissolve in water, forming transparent solutions, but when these imitation solutions are examined with a powerful microscope they are found to consist of separate particles drifting about in the liquid. Such mixtures are known as colloidal solutions. Gum, starch, gelatine, and glue form colloidal solutions. All gelatinous precipitates are really colloidal solutions.

167. Saturated solutions. A solution is said to be **saturated** when it contains all of a given solute which it can hold at a given temperature. That is, when there is a state of equilibrium between the dissolved substance and the solute.

If a soluble substance, such as sugar or salt, be placed in a tall vessel of water, it at once goes to the bottom and becomes surrounded at the bottom with a saturated solution. In the course of time the whole amount of water would become saturated, but if the solvent be stirred or shaken thoroughly a condition of saturation will be quickly reached.

To make a saturated solution of a solid, then, the solid should first be pulverized and added to the liquid with much shaking until there is a decided excess of the undissolved substance present. If all of the solute goes into solution it is evident that a saturated solution has not been obtained.

168. Supersaturated solutions. In general, hot liquids will dissolve more of a given substance than cold liquids. To make a hot saturated solution the simplest method is to heat the liquid to boiling and add the finely pulverized substance little by little, until there is a decided excess of the undissolved material present.

If the hot saturated solution be filtered and the filtrate cooled, some of the original solute usually separates from solution as a precipitate. The amount of precipitate is the difference between the amount of the substance contained in the hot and cold saturated solutions.

In case the excess of solute does not separate on cooling a hot saturated solution, the resulting cold solution is said to be **supersaturated.**

A supersaturated solution is one containing more of a given solute dissolved than should normally be contained in a cold saturated solution at the same temperature.

A supersaturated solution may be caused to form a precipitate by dropping in a minute piece of the original solid substance or by scratching the inside of the containing vessel with a glass rod.

169. Crystals and crystallization. The majority of chemical substances, both elements and compounds, when they are in the solid form, are found to exist in definite geometrical shapes known as crystals. These crystals are bounded by definite geometrical faces that reflect light.

170. Crystalline. A substance may be said to be crystalline, if it possesses naturally formed faces that reflect light. Any naturally formed substance that sparkles in the sunlight is crystalline. Sugar, salt, and snow are good examples. Any substance that is not crystalline is said to be amorphous. Glass and rosin are good examples of such substances.

171. Formation of crystals. If a cold solution of any crystalline substance be allowed to evaporate spontaneously, it will eventually become a cold saturated solution. If the evaporation then continues any further, crystals will begin to form. On account of the slow evaporation and consequent slow concentration of the solution, these crystals will grow rather large. If, on the other hand, the solution be concentrated by boiling, or the hot concentrated solution rapidly cooled, the crystals resulting are very minute, and may best be viewed under the microscope.

172. Crystal forms. Examination shows that all crystals may be divided into six classes in accordance with the manner in which the faces are arranged about certain imaginary axes.

(a) The regular system. In this system there are three axes, all of equal length and all at right angles to each other. The cube and octahedron are examples of the simplest forms belonging to this system. In the cube the axes pass through the centres of the opposite faces, and in the octahedron they go from corner to corner through the crystal.
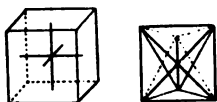
FIG. 33. REGULAR
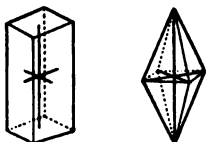
FIG. 34. TETRAGONAL
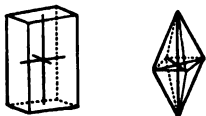
FIG. 35. ORTHO-RHOMBIC
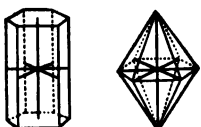
FIG. 36. HEXAGONAL
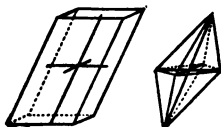
FIG. 37. MONO-CLINIC
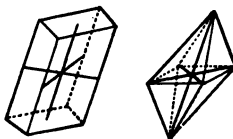
FIG. 38. TRI-CLINIC

See Fig 33. Common salt, galena, and garnet belong to this system.

(b) **The tetragonal system.** In this system there are two equal axes and one longer or shorter, all at right angles to each other. (See Fig. 34.)

Tin dioxide, cassiterite, belongs in this system.

(c) **The ortho-rhombic system.** Three axes, all unequal in length and all at right angles (Fig. 35). Sulphur, saltpetre, and magnesium sulphate (Epsom salt) belong in this system.

(d) **The hexagonal system.** Four axes, three in one plane all of the same length, making angles of sixty degrees with each other, and a fourth at right angles to all of these at their point of intersection (Fig. 36). Snow crystals, quartz, and sodium nitrate crystallize in the hexagonal system.

(e) **The mono-clinic system.** Three axes, two at right angles and a third perpendicular to one and inclined to the other (Fig. 37). Glauber's salt and green vitriol are examples of mono-clinic crystals.

(f) **The tri-clinic system.** Three axes, all inclined to each other (Fig. 38). Crystals of blue vitriol well illustrate this system.

173. Characteristics common to all crystals. Crystals of the same substance formed under similar conditions are always similar.

The angle between any two corresponding faces on two crystals of the same substance is always the same.

If the plane of any face when extended cuts more than one axis, the distances of these points of intersection from the common point of intersection of all the axes are proportional to the numbers 1, 2, 3, or 4. (See Fig. 39.)

174. **Water of crystallization (water of hydration).** Many substances when crystallizing from water solution combine with a definite quantity of water. This water seems to be necessary both for the crystal form and the color, if any. Such water is known as **water of crystallization,** or **water of hydration.** Compounds containing water of crystallization are also known as **hydrates. Blue vitriol,** crystallized copper sulphate, contains five molecules of water and is represented by the formula $CuSO_4$ $+ 5 H_2O$. Many substances combine with water in several different proportions; thus, copper sulphate also combines with one and three molecules of water, and in order to distinguish them they are referred to as the **mono-, tri-,** or **pentahydrate.**
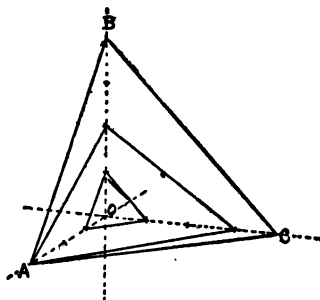
Fig. 39

Crystals containing water of crystallization give up the water when heated, leaving the original compound in the amorphous condition.

175. **Efflorescence.** Many substances containing water of crystallization lose part or all of this water when exposed to the air, at the same time losing their crystalline form and falling to amorphous powders. This process is known as **efflorescence.** In such cases the natural tendency of the water to evaporate from the crystal is greater than the normal pressure of the water vapor in the air. **Glauber's salt,** $Na_2SO_4 + 10 H_2O$, and **sal soda,** $Na_2CO_3 + 10 H_2O$, always act in this way. Blue vitriol in moist cold air does not effloresce appreciably, but in warm dry air readily loses some of its water.

176. **Deliquescence.** Many very soluble substances tend to absorb moisture from the air and ultimately dissolve in the water so absorbed. Such substances are said to be **deliquescent.** Calcium chloride, magnesium chloride, potassium hydroxide, and lithium chloride are good examples.

Questions

1. What limits a physical or chemical change in a given direction? (165).
2. How long will a liquid continue to evaporate in an enclosed space? (165).
3. What is a solution? a solute? a solvent? (166).
4. What is a colloidal solution? (166).
5. What is a saturated solution? a supersaturated solution? (167–168).
6. How may a supersaturated solution be caused to crystallize? (168).
7. What is meant by the terms crystalline and amorphous? (170).
8. Name the six classifications of crystal forms (172).
9. What is water of crystallization? (174).
10. What is meant by efflorescence and deliquescence?   And give examples of substances which commonly illustrate each (175–176).

CHAPTER XIII

Osmotic Pressure, Vapor Tension, Boiling-Points and Freezing-Points of Solutions

177. Osmotic pressure. Dissolved substances exert a pressure in solution which is exactly analogous to gaseous pressure. This pressure is, however, not appreciable, unless the solution is contained in a vessel provided with a **semipermeable membrane,** and the whole immersed in a vessel of the pure solvent. A semipermeable membrane allows the passage of the solvent, usually water, but does not allow much of the dissolved substance to pass through. Pressures produced in this way are known as **osmotic pressures.**

178. Illustration. Osmotic pressure may be demonstrated in many ways. If the stalk of a plant be cut near the ground, and a glass tube fastened on the stump so there is no possible leakage, the sap will rise to remarkable heights. This is due to the fact that the plant juices contain salts in solution forming a liquid more dense than water. The cell walls of the roots of the plant act as semipermeable membranes, and water enters until the hydrostatic pressure of the column of liquid in the tube is just equal to the osmotic pressure of the salts in solution.

The bell of a thistle tube may be filled with a strong sugar solution and covered by tying a piece of parchment or other animal membrane over the opening. If the parchment end be then immersed in pure water, the sugar solution will rise in the tube until equilibrium is established. (See Fig. 40.)
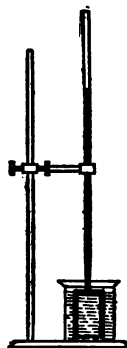
FIG. 40

179. Magnitude of the pressure. Osmotic pressure is analogous to gas pressure. If a gram-molecule (the molecular weight in grams) of solid carbon dioxide were placed in a closed vessel of 1-liter capacity, it would soon turn to the gaseous condition.

As a gram-molecule of any substance in the gaseous condition would occupy 22.4 liters at normal temperature and pressure, so this carbon dioxide would endeavor to expand to this volume, but, being enclosed in 1-liter volume, there would be 22.4 liters of gas compressed to 1 liter, which would produce a gaseous pressure of 22.4 atmospheres (216).

If a gram-molecular weight of any substance, such as sugar, which is undissociated in solution, be dissolved in 1 liter of water, it would show an osmotic pressure of 22.4 atmospheres. The molecular weight of sugar is 342, so that 342 g. dissolved in water would produce a pressure of 22.4 atmospheres. (An "atmosphere" means the pressure of the atmosphere at the sea-level, and equals a pressure of 760 mm., or about 15 lbs., per square inch.)

Less than the molecular weight of sugar would produce a proportionally less pressure. 34.2 g. of sugar would produce an osmotic pressure of exactly 1/10 of the above, at normal temperature. If the temperature were higher the pressure would be higher, strictly in accordance with Charles's law.

180. **Laws of osmotic pressure.** It should be noted that the following laws are identical with the laws of **Boyle, Charles,** and **Avogadro** (213).

(*a*) **With a fixed quantity of material in solution, at constant temperature the osmotic pressure varies inversely as the volume.**

(*b*) **With a fixed volume, and a fixed quantity of material in solution, the osmotic pressure is proportional to the absolute temperature.**

(*c*) **Equal volumes of the same solvent at the same temperature and showing equal osmotic pressures contain equal numbers of particles** (213).

181. **Computation of osmotic pressures.** One gram-molecule of any substance in the gaseous form at normal temperature and pressure occupies 22.4 liters.

The problem is to find what the pressure would be if 1 gram-molecule or fraction thereof of any material is placed in an osmotic cell at a given temperature.

The general gas law may be utilized:

$$\frac{P^\circ V^\circ}{T^\circ} = \frac{PV}{T}.$$

$P°$ is a pressure of 1 atmosphere.

$V°$ is the volume of the gram-molecule at normal temperature and pressure, equal to 22.4.

$T°$ is 273° absolute.

The expression then becomes:

$$\frac{PV}{T} = \frac{22.4}{273}.$$

P is the osmotic pressure, V the volume of the cell, and T the absolute temperature.

$$P = \frac{T}{V} \times \frac{22.4}{273}.$$

Example. What would be the osmotic pressure of 114 g. of sugar in 1 liter of water, at a temperature of 100° C.?

Substituting in the formula, we have:

$$P = \frac{373}{1} \times \frac{22.4}{273}.$$

This would give the pressure due to 1 gram-molecule of sugar. Since only 114 g. were used, the pressure would be $\frac{114}{342}$ as great.

182. Pressures produced by substances dissociated in solution (191). The osmotic pressures produced by very dilute solutions of binary salts and strong binary acids are found to be nearly twice as great as the pressure produced by the corresponding molecular quantity of sugar. This is due to the fact that these substances are almost completely dissociated in very dilute solution (193). This results in the production of twice as many particles and therefore twice the pressure.

183. Exercise. Compute the osmotic pressures in the following cases:

1. 10 g. of sugar in 1 liter of water at a temperature of 0° C.

2. 10 g. of sugar in 1 liter of water at a temperature of 273° C.

3. Hydrochloric acid is 90% dissociated in a solution containing .1 gram-molecule to the liter. What would be the osmotic pressure produced by 3.65 g. of hydrochloric acid in 1 liter of water at a temperature of 0° C.?

4. Assuming sodium hydroxide to be 90% dissociated in a solution containing .1 gram-molecule to the liter, what would be the osmotic pressure due to a solution of 4 g. in 1 liter of water at a temperature of 100° C.?

184. Vapor pressure of solutions. The vapor pressure of a solution of a substance is less than that of the pure solvent. This is because the presence of the molecules of the dissolved substance not only tends to prevent the escape of molecules of the solvent, but actually attracts some of those that have escaped back into the liquid.

If a solution of some substance in water be placed in the same enclosed space with some water, and the temperature be constant, the water will entirely evaporate and condense in the solution. This is because the vapor pressure over the solution can never become as great as the pressure over the water. Therefore equilibrium cannot be established until the water has entirely evaporated. As the space was enclosed, this can only take place as a result of the condensation of the vapor into the solution.

185. The boiling-point law. If different portions of the same solvent contain the same number of particles of dissolved substances per unit volume, the boiling-point will be raised by the same amount.

Assuming for the present that there is no dissociation in solution, this gives a very simple method of getting molecular weights. It is only necessary to find the elevation of the boiling-point produced by a gram-molecule of a known substance in a suitable solvent, then add to an equal volume of the same solvent sufficient of the unknown substance to produce the same elevation of the boiling-point. When this has been done 1 gram-molecule of the unknown substance must have been used.

186. The freezing-point law. Equal numbers of particles per unit volume in different portions of the same solvent produce equal depressions of the freezing-point. This again gives a method for determining molecular weights. It is only necessary to compare the depression of the freezing-point produced by a substance whose molecular weight is known with that produced by a definite weight of a substance whose molecular weight is desired.

187. Exercise. What will be the final condition of equilibrium in each of the following cases? Give the full explanation.

1. A liquid in an enclosed space at a constant temperature (165).

2. Two portions of the same liquid in an enclosed space at a constant temperature, one portion being above the other.

3. Two portions of the same liquid contained in the same enclosed space, at different constant temperatures (162).

4. A water solution of some substance in the same enclosed space with a vessel of water at constant temperature (184).

Questions

1. What is osmotic pressure? (177). Give an illustration.
2. What is osmotic pressure analogous to? (179).
3. What osmotic pressure would a gram-molecular weight of sugar dissolved in 1 liter of water show? (179).
4. State three laws of osmotic pressure (180).
5. What osmotic pressure would 2 g. of sugar dissolved in 100 c.c. of water show at a temperature of 22° C.? (181).
6. How is the osmotic pressure affected if the solute is dissociated in solution? (182).
7. What is the effect of the temperature on the osmotic pressure? (180).
8. How does the vapor pressure of a liquid vary with the temperature? (162).
9. What is the boiling-point? (162).
10. How is the vapor pressure of a liquid affected by the presence of dissolved substances? (184).
11. State the boiling-point law (185).
12. How could a molecular weight of a soluble substance be determined by means of the boiling-point law? (185).
13. What is the freezing-point law? (186).
14. How could the molecular weight of a soluble substance be determined by means of the freezing-point law? (187).
15. Could molecular weights be roughly determined by means of osmotic pressures? (180).

CHAPTER XIV

ELECTROCHEMISTRY

188. Dissociation. When a substance decomposes in such a way that the products may reunite to form the original material, it is said to **dissociate**. All such reactions are cases of what are termed reversible reactions. **The dissociation goes on until the concentrations of the products are such that the original substance is formed again just as fast as it is decomposed; that is, until a condition of equilibrium is reached.** In order to reach a condition of equilibrium it is usually necessary that the reaction take place in an enclosed space; for otherwise some of the products might escape, and the change would go on to completion.

Lime, CaO, is made by heating limestone, calcium carbonate, $CaCO_3$.

The products are CaO and CO_2. Ordinarily, the CO_2 goes off in the air and nothing but lime is left. If, however, the reaction were compelled to take place in a closed space, a condition would soon be reached where the recombination of the CO_2 and the CaO would exactly equal the decomposition of the limestone. The following equation indicates the change. The double arrow is used to indicate a reversible reaction:

$$CaCO_3 \leftrightarrows CaO + CO_2.$$

Other similar reactions are shown by the following equations:

$$H_2SO_4 \leftrightarrows H_2O + SO_3.$$
$$Ca(OH) \leftrightarrows H_2O + CaO.$$

189. Decomposition. Of course it is possible to decompose many substances in such a way that they cannot possibly reunite directly to form the original substance. Such changes are **decompositions** and should not be confused with dissociations. Potassium chlorate is decomposed by heating, and gives potassium chloride and oxygen.

$$2 KClO_3 = 2 KCl + 3 O_2.$$
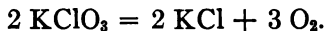
190. **Positive and negative electrification.** When any two different substances are rubbed together and separated, under the proper conditions, it is found that each has become electrified. This is shown by the fact that each piece of matter so treated will attract small particles of dust and bits of paper.

It is also found that the two pieces of matter are electrified with different kinds of electricity, and, when suspended in a manner so they are free to move, that they attract each other. Similar pieces of matter electrified in the same way repel each other. From this fact it is concluded that like kinds of electricity repel and unlike kinds attract. One kind is called positive electricity and the other negative.

191. **Electrolytic dissociation, or ionization.** There is reason to believe that when certain substances, such as acids, bases, and salts, are dissolved in water, the molecules of the dissolved substances are split apart by the water into at least two different kinds of particles, each charged with electricity, the one kind with positive and the other with negative. The total amount of the positive charges is exactly equal to the total amount of the negative.

These charged particles, which exist in solution, are known as **ions,** and the process by which they are formed by the action of the water is known as **electrolytic dissociation, or ionization.**

Substances which are capable of being ionized in solution are called **electrolytes.** The ions produced by electrolytes in solution are in many cases the same as the radicals forming the compound, except that they carry charges of electricity, the basic or positive radical carrying a positive charge and the acid or negative radical carrying a negative charge.

If a molecule contains several basic radicals and one or more negative radicals, it splits up at first into one positive ion, consisting of one charged basic radical, and one complex negative ion. On extreme dilution it would be split up into as many ions as it had radicals. Thus, we say sodium chloride, when put in solution in water, gives positive sodium ions and negative chlorine ions, represented as follows, the number and kind of charge being indicated by plus or minus signs:

$$NaCl \text{ dissolved} \leftrightarrows Na^+ + Cl^-.$$
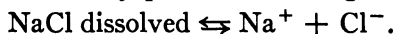
If the electrolyte contains more than two radicals, it breaks up first into only two, thus:

$$H_2SO_4 \text{ dissolved} \leftrightarrows H^+ + HSO_4^-.$$
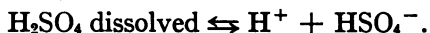
On further dilution it would break up as follows:

$$H_2SO_4 \text{ dissolved} \leftrightarrows H^+ + H^+ + SO_4^{--}.$$

It is understood that the total positive charge of all the positive ions is exactly equal to the total negative charge of all the negative ions.

192. Ionic equilibrium. Substances dissociate in solution until the rate of recombination of the ions is exactly equal to the rate of dissociation, and a condition of equilibrium is established. All dissociations of this kind are therefore reversible reactions, and should properly be represented by the use of the double arrow:

$$HCl \leftrightarrows H^+ + Cl^-.$$
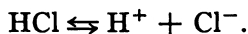
193. Degree of dissociation. The amount of dissociation necessary to produce equilibrium varies greatly for different substances.

All the strong acids and bases and all salts are almost completely dissociated in dilute solution.

Substances that are about 90% dissociated in a solution containing .1 gram-molecule per liter:

> Hydrochloric acid, HCl.
> Hydrobromic acid, HBr.
> Hydriodic acid, HI.
> Chloric acid, $HClO_3$.
> Bromic acid, $HBrO_3$.
> Nitric acid, HNO_3.
> Potassium hydroxide, KOH.
> Sodium hydroxide, NaOH.
> Barium hydroxide, $Ba(OH)_2$.
> Strontium hydroxide, $Sr(OH)_2$.

Some substances that are very slightly dissociated in solution:

> Water, H_2O.
> Carbonic acid, H_2CO_3.

Acetic acid, $HC_2H_3O_2$.

Hydrogen sulphide, H_2S.

Hydrocyanic acid, HCN.

Ammonium hydroxide, NH_4OH.

Boric acid, H_3BO_3.

Aluminum hydroxide.

Ferric hydroxide.

Zinc hydroxide.

Solution Pressure

194. Solution pressure. All metals when placed in liquids have a tendency to send off ions into the liquid. These ions carry positive charges of electricity, and the metal is left with a negative charge. The solution does not proceed very far in water, or in liquids that have no marked chemical action on the metal, on account of the attraction of the negatively charged metal for the positive ions. The tendency of a metal to send off ions into solution may be called its **solution pressure.** This pressure varies greatly with the different metals, platinum and gold having very low solution pressures, and sodium, magnesium, and zinc very high pressures.

195. Solution of metals in acids. Hydrogen itself may be considered to have a definite solution pressure. If a metal be immersed in an acid solution, it sends off ions into the solution. If the solution pressure of the metal is greater than the solution pressure of hydrogen, the charges on the hydrogen ions are neutralized by coming in contact with the negatively charged metal, and hydrogen gas is set free. More of the metal ions are set free, and the action continues until all of the metal is dissolved, all of the acid is destroyed, or the osmotic pressure of the metal ions is equal to the solution pressure of the immersed metal.

196. Precipitation of metals from solution. If a metal having a high solution pressure be placed in a solution of a metal having a lower solution pressure, the latter will be deposited in the metallic form on the immersed metal. Suppose a large piece of copper be placed in a solution of silver nitrate. The copper, having a higher solution pressure than the silver, will

send ions into solution; the silver ions will go to the copper plate, where they will give up their positive charges and appear as metallic silver. If sufficient copper is present, all of the silver will be thrown out of solution. The amount of the metal deposited will be the exact chemical equivalent of the amount of copper dissolved. In the case of the copper and silver, one atomic weight of copper, 63, would displace exactly two atomic weights of silver, or 216 weights.

197. The order in which the metals precipitate each other from solution. The names of the metals in the following series are arranged in the order in which they replace each other in solution, those at the top having the higher solution pressures and those at the bottom the lower. Any element in the series will replace all that follow it. Those above hydrogen will displace hydrogen from acids, while those below it, having lower solution pressures than hydrogen itself, will not do so.

Potassium	**Hydrogen**
Sodium	Bismuth
Barium	Copper
Strontium	Arsenic
Calcium	Mercury
Magnesium	Silver
Aluminum	Platinum
Manganese	Gold
Zinc	
Iron	
Cobalt	
Nickel	
Tin	

198. The simple galvanic cell, or battery. If two different metals be placed in the same liquid, they each send off ions. Each becomes negatively charged. If they be connected outside of the liquid by a wire, a current will be found to flow through the wire from the one having the lower solution pressure to the one having the higher. This is because the one having the higher pressure constantly sends ions into the solu-

tion, and hydrogen ions, or some other ions from the solution, are carried to the other metal, where they give up their charges and are set free (Fig. 41).

199. The Daniell cell. In this cell we have a zinc plate surrounded by zinc sulphate in one part of the jar, and a copper plate surrounded by a saturated solution of copper sulphate in another part. The two solutions are kept separate either by the force of gravity or by a porous cup. When the two plates are connected by a wire, the zinc, having the greater solution pressure, sends off zinc ions into the solution, thereby forcing the copper ions to the copper plate, where they give up their electrical charges and appear as a deposit of metallic copper (Fig. 42).

FIG. 41
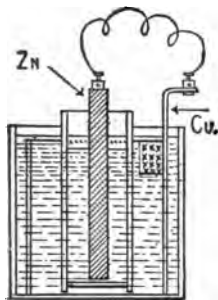
200. A simple concentration cell. In general, a current of electricity will be produced, if two pieces of the same metal are so arranged in a cell that one is surrounded with a strong and the other with a weak solution of a salt of that metal.

Let Fig. 43 represent such an arrangement, the side A containing a silver plate surrounded by a strong solution of silver nitrate and the side B a silver plate surrounded by a weak solution. On the side A there is a greater pressure of silver ions against the plate than there is on the side B. No great amount of silver can be deposited, however, on account of the inability of the positive charge to leave the plate. If the two plates be connected by a wire, the excess of positive charge from the side A is carried over to the side B, and more silver is deposited on the plate A. The plate B thereupon sends silver ions into solution. A current will continue to flow through the wire until the concentration of the silver nitrate is the same on both sides.

FIG. 42
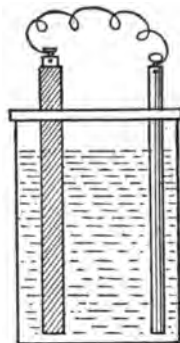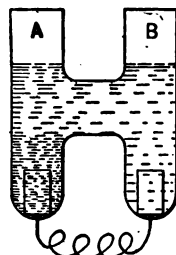
FIG. 43

Passage of the Electric Current through Liquids

201. Definitions. Electrolyte, any substance which, in the melted or dissolved condition, will allow the passage of the electric current.

Electrodes, the terminals immersed in a liquid.

The **positive electrode** is the one by means of which the current enters the liquid, called also the **anode.**

The **negative electrode** is the one by means of which the current leaves the liquid, called also the **cathode.**

202. Conductivity of solutions. Only solutions containing ions will conduct the electric current. If the solvent does not produce electrolytic dissociation in the solute, the current will not pass through it. The common solvent is water, but other liquids have the power of bringing about ionization. Pure water is almost completely undissociated, and therefore virtually does not conduct the current. A small quantity of the common acids, bases, and salts dissolved in water, however. renders it a good conductor.

203. Electrolysis of sodium chloride solution. Electrolysis is the process of decomposing a melted or dissolved substance by means
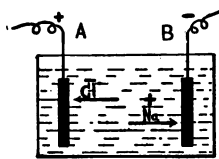
Fig. 44

of the electric current. Let Fig. 44 represent a vessel containing a dilute solution of sodium chloride, and let A be the positive electrode and B the negative electrode; then:

(1) A will have a positive charge and B a negative charge, because they are in contact with a source of electric current.

(2) When the salt was dissolved it was dissociated by the water into positive sodium ions and negative chlorine ions.

(3) Since unlike kinds of electricity attract each other, the chlorine ions will drift toward the positive electrode, give up their negative charge, and become nascent, or atomic chlorine. These soon unite with each other, forming molecular or gaseous chlorine, which is set free.

Since the solution contains some hydrogen ions from the water, and since hydrogen has a less solution pressure than sodium, the hydrogen ions undoubtedly go to the negative

electrode, where they lose their charges and are set free. If it is assumed that the sodium also goes to the negative electrode and becomes discharged, it must react with the water to form sodium hydroxide and hydrogen:

$$2 \, Na + 2 \, HOH = 2 \, NaOH + H_2.$$
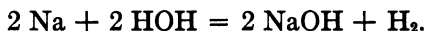
If the positive ion is a metal that does not react with the liquid, it is generally thrown out of solution in the form of a deposit on the electrode. This principle is made use of in electroplating.

If the negative ion is a single atom, it is generally set free; if it is complex, like SO_4, NO_3, etc., it reacts with the water to form an acid, and oxygen is set free.

Thus:

$Cu(NO_3)_2$ gives the ions Cu^{++} and $NO_3^- + NO_3^-$.

The copper is deposited on the negative electrode in the metallic form and the nitrate reacts with the water according to the equation:

$$4 \, NO_3 + 2 \, H_2O = 4 \, HNO_3 + O_2.$$
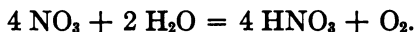
204. Exercise. Write equations showing all changes involved in the electrolysis of the following compounds:

Hydrochloric acid, nitric acid, sulphuric acid, sodium sulphate, sodium chloride, sodium nitrate, sodium hydroxide, cupric chloride, cupric nitrate, cupric sulphate, silver nitrate, and silver sulphate.

205. Faraday's law. **If any number of electrolytic cells, each containing different electrolytes, be connected in series and a current passed through them all, the actual quantities of the various elements set free will be proportional to the corresponding chemical equivalents of those elements.**

Let us assume that the elements so set free were oxygen, hydrogen, copper, silver, lead, zinc, mercury, and chlorine, and that 16 weights of oxygen were formed in the first cell.

Then there would have been formed at the same time 2 weights of hydrogen, 63.6 of copper, 216 of silver, 206.9 of lead, 65.4 of zinc, 200 of mercury, and 71 of chlorine. In other words, **the quantity of each element set free is proportional to its atomic weight divided by its valence.**

Questions

1. What is meant by dissociation? (188).
2. What limits the extent of dissociation in any case? (188).
3. How does decomposition differ from dissociation? (189).
4. What kinds of electricity attract? repel? (190).
5. What is meant by electrolytic dissociation? (191).
6. What is an ion? an electrolyte? Is electrolytic dissociation complete?
7. What is meant by ionic equilibrium? (192).
8. Mention several classes of substances which are highly dissociated in solution; some substances which are only slightly dissociated (193).
9. What is meant by solution pressure? Name some metals having high solution pressures; some with low pressures (194).
10. Explain the solution of metals in acids. What metals dissolve in acids with the evolution of hydrogen? (195).
11. What metals displace other metals from solutions of their salts? (196).
12. Give the order of activity of the metals (197).
13. Explain the action of a simple galvanic cell (198).
14. Describe a simple concentration cell (200).
15. Define the terms electrolyte; electrolysis; electrode; positive electrode; negative electrode; anode; cathode (201).
16. Explain the electrolysis of sodium chloride solution (203).
17. State Faraday's law (205).

CHAPTER XV

THERMOCHEMISTRY

206. Specific heat. Different substances have different powers or capacities for absorbing heat. The same amount of heat applied to equal weights of different substances will not raise the temperatures to the same degree. **Specific heat is the ratio of the amount of heat necessary to raise the temperature of a certain weight of a substance 1° to the amount of heat necessary to raise the temperature of an equal weight of water 1°.** The specific heat of copper is .0952, of silver .057. (See Table No. VII, page 243.)

207. Heat units. The amount of heat necessary to raise the temperature of 1 kilogram of water from 0° to 1° is 1 **large calorie.** A **small calorie** is one one-thousandth of a large calorie. In what follows in the book the numbers refer to the large calorie.

208. The law of DuLong and Petit. The product of the specific heat of an element in the solid state by its atomic weight is approximately equal to 6.4. This product is known as the **atomic heat.**

Element	Specific heat	Atomic weight	Atomic heat
Gold...............	.0324	197.2	6.40
Zinc...............	.0955	65.4	6.20
Nickel............	.1080	68.7	6.30
Iron...............	.1140	55.9	6.37
Lead...............	.0314	207.0	6.50

The above principle gives us a rough method for determining the atomic weights of those elements the specific heats of which have been determined. It is only necessary to divide the constant 6.4 by the specific heat; the result is approximately the atomic weight. (See Table VI, page 241.)

209. Heat of formation. Every chemical change is accompanied by some manifestation of energy; that is, there is an evolution or absorption of heat, light, or electricity. This manifestation is commonly evident as heat. The amount of heat formed in a reaction is just as much a product of the change as any of the substances formed and should properly appear in the equation. The **heat of formation** is the number of calories that are set free or absorbed when 1 gram-molecule of a substance is formed from the elements.

$$H_2 + Cl_2 = 2\,HCl + 22\ cal.$$
$$2\,K + S = K_2S + 101\ cal.$$
$$2\,H_2 + O_2 = 2\,H_2O + 68\ cal.$$
$$H_2 + S + 2\,O_2 = H_2SO_4 + 190\ cal.$$
$$2\,Na + S + 2\,O_2 = Na_2SO_4 + 328\ cal.$$
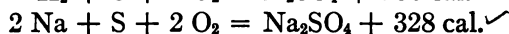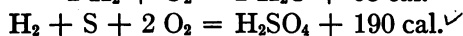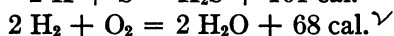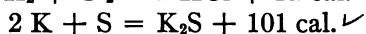
The values of other heats of formation are given in Table VII (282). **Heat of decomposition** is the number of calories which are absorbed or set free when a gram-molecule of a compound is decomposed into its elements. This heat is numerically equal to the heat of formation. An **exothermic compound** is one during the formation of which from the elements heat was given out. An **endothermic compound** is one during the formation of which from the elements heat was absorbed.

210. Heat of reaction. When heat is evolved during a chemical change the reaction is said to be **exothermic**; when heat is absorbed it is said to be **endothermic**. When one molecular weight of sodium hydroxide is neutralized by one molecular weight of hydrochloric acid, 13.7 calories of heat are set free.

$$NaOH + HCl = NaCl + HOH + 13.7\ cal.$$
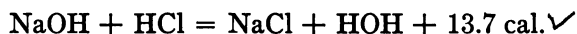
When molecular quantities of nitrogen and oxygen unite to form nitrous oxide, 17.4 calories are absorbed.

$$2\,N_2 + O_2 = 2\,N_2O - 17.4\ cal.$$

The heat of reaction is equal to the difference between the algebraic sum of the heats of formation of the factors and the heats of formation of the products.

$$NaOH\quad +\quad HNO_3\quad =\quad NaNO_3\quad +\quad HOH\ +\ 13.4\ cal.$$
111.8 cal.   49.1 cal.   106.3 cal.   68 cal.
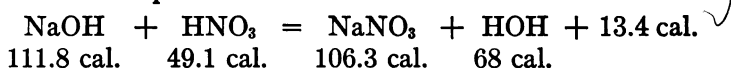
The heat of formation will vary according to the state in which the substance exists in the reaction. (See Table VII (282).)

211. **Exercise.** Making use of the values in Table VII, work out the heats of reaction in the following cases:

Sodium oxide, solid, with sulphur trioxide, solid.

Nitrogen pentoxide, solid, with sodium oxide, solid.

Sodium hydroxide, dissolved, with hydrochloric acid, dissolved.

Zinc with sulphuric acid, dissolved.

Example. What will be the heat of reaction if potassium is dissolved in hydrochloric acid?

K (solid) + HCl (dissolved) = KCl (dissolved) + H (gas).
       39.3 cal.   101.2 cal.
            101.2 − 39.3 = 61.9 cal.

Questions

1. What is specific heat? a large calorie? a small calorie? (206–207).
2. State the law of DuLong and Petit. How is this law made use of in determining atomic weights? (208).
3. What is heat of formation? heat of decomposition? (209).
4. What is heat of reaction and how may it be estimated? (210).
5. Making use of the table of heats of formation, find the amounts of the heats of reaction of the bases with the acids. Note whether or not it is nearly a constant for each molecule of water formed (211).

CHAPTER XVI

Molecular and Atomic Weights, Derivation of Formulas

212. Gay Lussac's law of combining volumes. When two or more gases unite to form a compound, the volumes of the gases concerned bear a simple relation to each other. If the product is a gas its volume bears a simple relation to the volumes of the factors.

$$H_2 + Cl_2 = 2\,HCl.$$
1 vol.　　1 vol.　　2 vols.

$$2\,H_2 + O_2 = 2\,H_2O.$$
2 vols.　　1 vol.　　2 vols.

$$3\,H_2 + N_2 = 2\,H_3N.$$
3 vols.　　1 vol.　　2 vols.
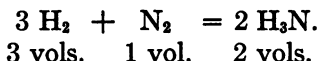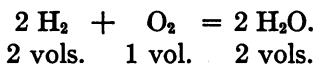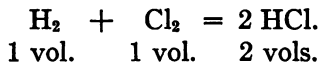
213. Avogadro's hypothesis. Equal volumes of all gases at the same temperature and pressure contain the same number of molecules.

Or, in other words, all gaseous molecules under the same conditions occupy equal volumes of space.

If an equation has been properly written so that each symbol represents a molecule, then, from the above principle, the relative volumes of the various substances entering that reaction, when considered to be in the gaseous form, are proportional to the number of molecules as indicated by the coefficients in the equation.

Example. How many liters of oxygen would be required to burn 10 liters of alcohol vapor?

$$C_2H_5OH + 3\,O_2 = 2\,CO_2 + 3\,H_2O.$$
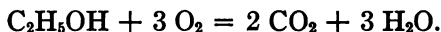
This equation means that 1 molecule of alcohol requires 3 molecules of oxygen to burn it, and results in the formation of 2 molecules of carbon dioxide and 3 molecules of water.

In other words, 10 liters of alcohol vapor require 30 liters

of oxygen to burn it and form 20 liters of carbon dioxide and 30 liters of water vapor.

214. Exercise. Write equations showing the oxidation, or burning, of gases, and show how many liters of the various products would be formed if 10 liters of the gas were used (255).

215. Gram-molecule. The weight of a substance in grams equal to its molecular weight is known as a gram-molecule. 1 gram-molecule of oxygen is 32 g. of the gas; of hydrogen is 2.016 g.; of carbon dioxide is 44 g. A moment's consideration will show that all gram-molecular weights contain the same number of molecules, for the ratio of any two such weights must be the same as the ratio of the corresponding molecular weights.

216. Gram-molecular volume. The volume occupied by a gram-molecule of any substance in the gaseous condition and at normal temperature and pressure is equal to 22.4 liters. This volume is a constant and is known as the **gram-molecular volume.** The student will be impressed with this fact if he divides the molecular weights of the common gases by the known weight of a liter of each.

217. Molecular weights of gases. In order to determine the molecular weight of a gas it is only necessary to determine the weight of a given volume and calculate the weight of the gram-molecular volume, 22.4 liters in grams. This number will be numerically equal to the molecular weight. In other words, the weight of the gram-molecular volume of any substance in grams, at normal temperature and pressure, is numerically the same as its molecular weight.

218. Determination of the weight of a liter of a gas. A glass balloon similar to that indicated in Fig. 45, and having a capacity varying from 100 c.c. to 1000 c.c. is filled with a gas and weighed. The balloon is now

Fig. 45

entirely exhausted by means of a mercury air-pump and weighed again. The difference between these two weights is the weight of the gas. The volume of the balloon being known, it is a simple matter to calculate the weight of a liter. The buoyant
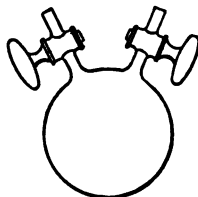
effect of the atmosphere during the weighing is the same in both cases and does not affect the result.

219. Molecular weights of solids. Many substances are not readily converted to the gaseous condition and therefore the weight of the gram-molecular volume cannot be determined. In such cases it is possible to ascertain the approximate molecular weight by the boiling-point, freezing-point, or osmotic-pressure methods (**180**). It will be recalled that equal volumes of the same liquid show equal elevations of the boiling-point, depressions of the freezing-point, and equal osmotic pressures, when they contain equal numbers of particles in solution. A gram-molecular weight of a known substance will produce a certain elevation of the boiling-point. It is only necessary to add sufficient of the unknown substance to an equal volume of the same solvent until the boiling-point has been raised· the same amount. The amount of the substance so added will be 1 gram-molecule. Of course allowance must be made for possible electrolytic dissociation (**191**).

220. Gas and vapor densities. By density is ordinarily meant the amount of matter in a cubic centimeter of the substance. The gas density of hydrogen according to this would be .0000896. In the study of chemistry, the term "gas density" is used to mean the ratio of the weight of a given volume of a gas to the weight of an equal volume of some standard gas. The standard gas now used for reference is a hypothetical substance one-sixteenth as heavy as oxygen. To obtain a gas density, therefore, it is necessary to divide the weight of a given volume of the gas by the weight of an equal volume of oxygen at the same pressure and temperature, and multiply the result by 16. **Vapor density** is the same as gas density, but is applied to substances which do not ordinarily exist in the gaseous form.

221. The molecular weight of a substance is equal to twice its gas density. The gas density, when determined as indicated in the last paragraph, is a number which shows how many times heavier a molecule is than one-sixteenth of an oxygen molecule. Since the molecular weight of oxygen is 32, one-sixteenth of it is 2. The gas density, then, is a number which shows how many times heavier the molecule of a gas is than an imaginary mole-

cule which weighs 2. The actual molecular weight would there-
fore be equal to twice the gas density.

**222. Molecular weights of substances which can be readily con-
verted to the vapor condition. Victor Meyer's method.**

In this method a small quantity of the substance is vaporized,
and the volume of air displaced by the vapor is measured.

This volume is reduced to the corresponding volume at $0°$
C. temperature and 760 mm. pressure and multiplied by the
weight of 1 c.c. of oxygen under the same condi-
tions (160). The ratio of the weight of the sub-
stance taken to this weight shows how many times
heavier the molecule is than 1 molecule of oxygen.
This result, multiplied by 16, gives the vapor density
of the material. The apparatus used is indicated
in Fig. 46. It consists of two glass tubes. The
outer one has a bulb at the bottom in which is
placed some liquid that has a higher boiling-point
than that of the substance to be vaporized. The
vapor-density tube is suspended in this and the
liquid in the outer tube heated to boiling. After
the air in the inside tube has ceased to expand, the
end of the delivery-tube at E is placed under an
inverted measuring-tube, F, full of water. About 1/10 g. of
the substance is placed in a small glass-stoppered vial and
carefully weighed. The cork, at D, is removed, the vial dropped
in, and the cork quickly replaced. The vial passes through
the long inner tube to the enlarged portion at C. The heat
causes the material to vaporize, the stopper is blown out, and
a volume of air escapes into the graduated tube F just equal
to the volume of the vapor.
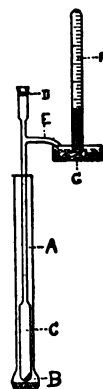
Fig. 46

**223. Determination of the formula from the analysis and molecular
weight.** Suppose a new substance is found and it is desired
to determine its formula. It is first analyzed and its chemical
composition ascertained in per cents. Then its molecular
weight is determined.

If each percentage be divided by the corresponding atomic
weight, a series of numbers will be obtained which will be pro-
portional to the numbers of the different atoms in the molecule.

If this series be divided by the smallest number, the results expressed as fractions and then reduced to a common denominator, the numerators will be the numbers of atoms of each element corresponding to the simplest formula.

Example. Suppose a substance contained carbon, 33.70%; hydrogen, 3.38%; oxygen, 62.92%; what would be the formula corresponding?

Dividing these per cents by the corresponding atomic weights, we have:

$$\frac{33.70}{12} = 2.81; \quad \frac{3.38}{1} = 3.38; \quad \frac{62.92}{16} = 3.93.$$

This means that the formula must be:

$$C_{2.81} \ H_{3.38} \ O_{3.93}.$$

Dividing each of these sub-numbers by the smallest and expressing the results as fractions, we have:

$$C_1 \ H_{1 \ 1/5} \ O_{1 \ 2/5}.$$
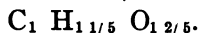
This means that there are one and one-fifth as many hydrogen atoms, and one and two-fifths as many oxygen atoms, as there were carbon atoms. This could only be the case if the formula were $C_5H_6O_7$.

If the molecular weight corresponding to this formula agrees with that found, then this formula is the correct one. Otherwise it is the simplest possible formula, and some multiple of it will correspond to the molecular weight.

If the molecular-weight determination is exact, it may be multiplied at once by the various percentages, and the results, divided by the atomic weights, will give the correct formula.

224. Exercise. Determine the simplest formulas corresponding to the following analyses:

1. Lead, 86.60%; sulphur, 13.40%.
2. Calcium, 51.10%; fluorine, 48.90%.
3. Mercury, 84.90%; chlorine, 15.10%.
4. Arsenic, 75.80%; oxygen, 24.20%.
5. Hydrogen, 1.59%; nitrogen, 22.22%; oxygen, 76.19%.
6. Iron, 70.00%; oxygen, 30.00%.

225. Exercise. Determine the correct formulas corresponding to the following analyses and molecular weights:

	Carbon	Hydrogen	Nitrogen	Oxygen	Molecular Weight
1.	91.30%	8.70%	....	....	91.8
2.	85.71%	14.29%	....	....	70.0
3.	54.55%	9.09%	....	36.36%	132.0
4.	40.00%	6.67%	....	53.33%	60.0
5.	92.30%	7.70%	....	....	52.0
6.	77.32%	7.63%	15.05%	....	93.0

226. **Determination of atomic weights.** An atom is the smallest particle of an element known to form part of a molecule. An atomic weight is numerically the same as the smallest weight in grams contained in a gram-molecular volume of any of its gaseous compounds at normal temperature and pressure. The determination of the atomic weight of an element that forms gaseous compounds is as follows:

(1) The weight of a liter of each of its gaseous compounds is determined.

(2) This weight multiplied by 22.4 gives the weight in grams of the gram-molecular volume.

(3) Each substance is carefully analyzed and the percentage of the required element is determined.

(4) The weight of the gram-molecular volume is multiplied by the percentage of the element, giving the number of grams of the element in each gram-molecular volume.

(5) The smallest of these weights will be numerically the same as the atomic weight.

The following table illustrates the method for chlorine:

Compounds ot Chlorine	Gram-Molecular Weight of Compound	Per cent of Chlorine in Compound	Grams of Chlorine in the Gram-Molecular Weight of Compound
Hydrogen chloride.........	36.50	97.26	35.5
Methyl chloride............	50.50	70.30	35.5
Methylene chloride.........	99.00	71.72	71.0
Mercuric chloride.........	271.00	26.20	71.0
Chloroform...............	59.25	89.87	106.5
Carbon tetrachloride.......	154.00	92.21	142.0

If the compound examined does not normally exist in the gaseous form, its molecular weight may be obtained from its vapor density (**222**).

In the above table, 35.5, being the smallest weight of chlorine in grams contained in a gram-molecular weight of any of its known gaseous compounds, is numerically the same as the atomic weight.

227. Accuracy of the method. In the above method the accuracy of the atomic weights depends upon the accuracy of the molecular weights. As these cannot be determined with very great accuracy, the exact weights are determined by the analysis of compounds of the element, which can be prepared in a state of great purity. The analysis of pure sodium chloride gives: sodium, 39.34%, and chlorine, 60.66%. These numbers, divided by the actual or approximate atomic weights, will give results showing the relative number of atoms in the molecule. The atomic weight of sodium being known as 23 and that of chlorine being assumed to be near 35.5, we divide the above per cents by these numbers:

$$\frac{39.34}{23} = 1.71; \ \frac{60.66}{35.5} = 1.71.$$

Since these two results are the same, we know the molecule contains the same number of sodium and chlorine atoms. Let X represent the true atomic weight of chlorine; then the ratio of the true atomic weight of chlorine to the true atomic weight of sodium is the same as the ratio of the per cent of chlorine to the per cent of sodium:

$$\frac{X}{23} = \frac{60.66}{39.34}, \text{ from which } X = 35.46.$$

228. Atomic weights of solid elements. Approximate atomic weights of the elements that do not form compounds readily converted to the gaseous condition may be obtained by dividing the constant, 6.4 (see **208**), by the specific heat of the element. Thus, the specific heat of gold is .0324; 6.4 divided by this number gives 196.6, which is very nearly the actual atomic weight.

229. Exact determination of atomic weight. The analysis of auric chloride gives: gold, 64.69%; chlorine, 35.04%. It is

now necessary to determine the relative numbers of atoms in the molecule. The above percentages are divided by the approximate and real atomic weights of the two elements. This gives the relative numbers of the atoms present. From the previous paragraph we have the approximate atomic weight of gold, 196.6; the known atomic weight of chlorine is 35.46.

$$\frac{64.96}{196.6} = .33 \text{ and } \frac{35.04}{35.46} = .99.$$

It is plain from an inspection of these results that there are three times as many atoms of chlorine in the molecule as there are atoms of gold. Let X be the actual atomic weight of gold; then the ratio of X to three atomic weights of chlorine must be the same as the ratio of the per cent of gold to the per cent of chlorine. That is:

$$\frac{X}{3 \times 35.35} = \frac{64.96}{35.04}, \text{ from which } X = 197.2.$$

230. The periodic arrangement of the elements. If all the elements be laid out in a row according to their increasing atomic weights, it will be noticed that certain properties recur at definite intervals. Leaving hydrogen and the rare gases of the atmosphere out of account and beginning with lithium, we have a silver-white metal with strongly basic properties. The eighth element is sodium, another silver-white metal with strong basic properties. As we proceed along the line we find that the metallic and basic properties decrease up to a certain point and then begin over again. The seventh element from lithium is fluorine, a gaseous non-metal. The seventh from sodium is gaseous chlorine. The next element after chlorine is metallic potassium. Not only do the physical properties of the elements recur at stated intervals, but the chemical reactions they admit of are similar. If we break our line of elements into lengths containing seven elements and arrange these lengths directly under one another, we find that similar elements fall into vertical columns. When this is done carefully, care being taken to see that elements having similar properties fall in the same vertical column, a table is obtained which is known as the **periodic arrangement** of the elements. This arrangement was first made by Mendelejeff in 1869.

231. **Table showing the periodic arrangement of the elements.**   (A few of the rare elements are omitted).

$$H = 1.008$$

0	I	II	III	IV	V	VI	VII	VIII		
R	RH R_2O	RH_2 RO	RH_3 R_2O_3	RH_4 RO_2	RH_3 R_2O_5	RH_2 RO_3	RH R_2O_7	RO_4		
He 3.99	Li 6.94	Gl 9.1	B 11.0	C 12.0	N 14.01	O 16.0	F 19.0			
Ne 20.2	Na 23.0	Mg 24.32	Al 27.1	Si 28.3	P 31.04	S 32.07	Cl 35.46			
A 39.88	K 39.10	Ca 40.07	Sc 44.1	Ti 48.1	V 51.00	Cr 52.00	Mn 54.93	Fe 55.84	Co 58.97	Ni 58.68
	Cu 63.57	Zn 65.37	Ga 69.9	Ge 72.5	As 74.96	Se 79.2	Br 79.92			
Kr 82.92	Rb 85.45	Sr 87.63	Y 89.0	Zr 90.6	Cb 93.5	Mo 96.0		Ru 101.7	Rh 102.9	Pd 106.7
	Ag 107.88	Cd 112.4	In 114.8	Sn 119.0	Sb 120.2	Te 127.5	I 126.92			
Xe 130.2	Cs 132.81	Ba 137.37	La 139.0	Ce 140.25						
					Ta 181.5	W 184		Os 191.0	Ir 193.0	Pt 194.8
	Au 197.2	Hg 200.6	Tl 204.0	Pb 207.1	Bi 208.0					
		Ra 226.4		Th 232.4		U 238.5				

232. **The periodic law.**   Elements in the same vertical column have similar properties, but the property increases or decreases with the atomic weight.   Thus, in the seventh group we have the halogen elements, F, Cl, Br, and I.   These elements all combine with hydrogen forming the corresponding halogen acids.   HF is very stable; HCl can be broken into the two elements without great difficulty; HBr is more unstable, and HI is very unstable.   **The attraction of the halogens for hydrogen decreases with increasing atomic weight.**   It is just the reverse

with regard to the attraction of the halogens for oxygen. Fluorine forms no compound with oxygen, while the oxide of iodine is very stable.

The properties of the elements are periodic functions of their atomic weights. It is even possible to predict the properties of an element which has not yet been discovered, provided there is a blank space in the table for it. Mendelejeff predicted the discovery and described the properties of several elements long before they were actually found. The table (231) gives the elements according to the periodic arrangement.

Questions

1. State Gay Lussac's law of combining volumes (212).
2. State Avogadro's hypothesis (213).
3. How many liters of oxygen would be necessary to burn 10 liters of marsh-gas completely to carbon dioxide and water vapor, and how many liters of each of the products would be formed? (213).
4. What is a gram-molecule? (215); the gram-molecular volume? (216).
5. How may the molecular weights of gases be determined? (217).
6. How is the weight of a liter of a gas measured? (218).
7. How may the molecular weight of a solid which is not readily converted to the gaseous condition be determined? (219).
8. What is gas density? vapor density? (220).
9. What relation does the molecular weight of a substance bear to its gas or vapor density? (221).
10. Describe Victor Meyer's method for the determination of vapor densities (222).
11. How may a formula be determined from the analysis and molecular weight of the substance? (223).
12. How are atomic weights approximately determined? (226).
13. How is an atomic weight accurately determined? (227).
14. What is an atomic weight? (226).
15. Some elements do not form compounds readily converted to the gaseous condition. How may the atomic weights of such elements be approximately determined? (228).
16. Describe the periodic arrangement of the elements (230).
17. State the periodic law (231).
18. Give the symbols and names of the common elements in groups according to the periodic arrangement (232).

CHAPTER XVII

Chemical Equilibrium and the Law of Mass Action

The terms "chemical equilibrium" and "mass action" have already been referred to several times in the earlier parts of this book, but it seems desirable to review the whole field at this point.

233. Chemical equilibrium. Every chemical change will continue in a given direction until a definite condition of equilibrium is established. This will be the case when the velocity of combination of the factors is exactly balanced by the velocity of the products reforming the factors.

In this sense all reactions are reversible.

If A and B enter into reaction to produce two other substances C and D, then there will be in the final condition not only some of C and D but also some of A and B.

If it is desired to represent the possibility of a reversed reaction taking place, it is customary to substitute a double arrow for the equality sign, thus:

Examples:

$$A + B \leftrightarrows C + D.$$
$$C + H_2O \leftrightarrows CO + H_2.$$
$$Na_2SO_4 + 2\ HCl \leftrightarrows 2\ NaCl + H_2SO_4.$$
$$H_2S + ZnCl_2 \leftrightarrows ZnS + 2\ HCl.$$
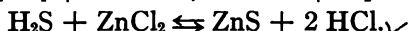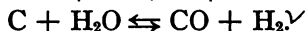
234. Completed reactions. If any of the products of a reaction be allowed to escape from the system, or if any are formed that are incapable of producing a reversed reaction, the original action goes on endeavoring to establish the required equilibrium until the original reaction is virtually complete.

Example 1. Precipitates. If one of the compounds formed in solution is insoluble, it will separate at once as a precipitate, the equilibrium will be destroyed, and more of the factors will combine until one of them is entirely used up:

$$BaCl_2 + K_2SO_4 = BaSO_4 + 2\ KCl.$$
$$CaCl_2 + Na_2CO_3 = \overline{CaCO_3} + 2\ NaCl.$$
$$Cu(NO_3)_2 + H_2S = \overline{CuS} + 2\ HNO_3.$$
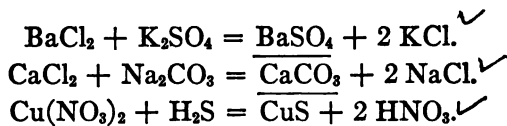
Example 2. One of the products may be volatile at the temperature at which the reaction takes place, in which case it will escape in the form of a gas and allow the reaction to proceed to completion:

$$Na_2CO_3 + 2\ HCl = H_2O + CO_2 + 2\ NaCl.$$
$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$
$$KCN + HCl = KCl + HCN.$$
$$Na_2SO_3 + 2\ HCl = 2\ NaCl + SO_2 + H_2O.$$
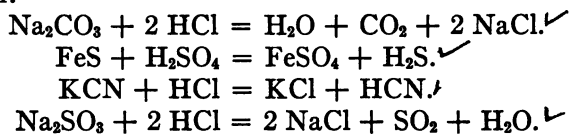
Example 3. One of the products may be water. In this case the water may or may not produce a reversed reaction. In most of the cases of neutralization of an acid by a base the water formed cannot reproduce the acid and base by its action on the salt:

$$NaOH + HCl = NaCl + HOH.$$
$$H_2SO_4 + 2\ NaOH = Na_2SO_4 + 2\ HOH.$$
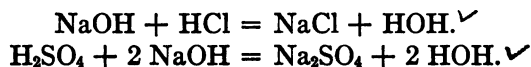
The Law of Mass Action

235. The above examples are all special cases illustrating the law of mass action. According to this law, when a reaction has reached a condition of equilibrium the ratio of the products of the concentrations of the substances on the two sides of the equation is always equal to a constant, no matter what the concentration was at the start. This is strictly true only of equations containing one molecule of a kind.

By concentration is meant the number of molecular weights per liter.

A substance A reacts with B to form C and D. Let a, b, c, and d represent the resulting concentrations. The equation representing the reaction would be:
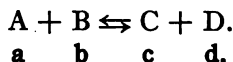
$$A + B \leftrightarrows C + D.$$
$$a \quad b \quad c \quad d.$$

According to the law, then:

$$\frac{ab}{cd} = k,$$

a constant. This constant will vary with the chemical affin-
ities involved and with the temperature.

If the equation indicated two or more molecules of any one
of the substances, the concentration would have to be raised to
the corresponding power. Thus, if there were two molecules
of A, the expression would become:

$$\frac{a^2b}{cd} = k.$$

The law admits of almost universal application to chemical
reactions as well as physical. The following examples illus-
trate its application:

236. Example 1. Solution of gases in liquids. Consider the case
of the solution of nitrogen in water:

$$N_2 \text{ gas} \leftrightharpoons N_2 \text{ dissolved.}$$

When a condition of equilibrium has been reached the ratio
of the concentration of the nitrogen in the gaseous form to the
concentration in the dissolved form must be a constant.

What would be the effect of increasing the pressure on the gas?

That is, in the expression

$$\frac{a}{b} = k,$$

if we increase a, what must happen to b in order that k remain
the same? Evidently b must increase in proportion. In other
words, if the pressure of a gas in contact with a liquid be
increased, more of the gas will dissolve in the liquid. The fol-
lowing law is a direct consequence of the law of mass action:

**Henry's law. At a given temperature the amount of gas that dis-
solves in a liquid is proportional to the pressure.** This does not
hold for those gases that are extremely soluble, such as ammo-
nia, hydrochloric acid, etc.

237. Example 2. A liquid in equilibrium with its vapor:

$$\underset{a}{H_2O \text{ vapor}} \leftrightharpoons \underset{b}{H_2O \text{ liquid.}}$$
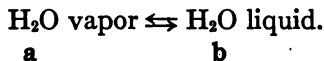
$$\frac{a}{b} = k.$$

Since the concentration of the water cannot be changed, the
concentration of the vapor cannot be altered. Any attempt to

increase it results in transforming some of it to the liquid condition.

238. Example 3. A solid in contact with its solution:
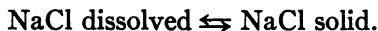
$$\text{NaCl dissolved} \leftrightarrows \text{NaCl solid.}$$
$$\text{a} \qquad\qquad\qquad \text{b}$$

Since the concentration of the solid cannot be changed, **b** is a constant; therefore **a** cannot be changed. Any attempt to increase the concentration of **a,** by reducing the volume of the liquid, results in causing some of the salt to crystallize.

239. Example 4. Dissociation of ammonium chloride. If ammonium chloride be heated, it is broken up into ammonia and hydrochloric acid:

$$\text{NH}_4\text{Cl} \leftrightarrows \text{NH}_3 + \text{HCl.}$$
$$\text{a} \qquad\quad \text{b} \qquad \text{c}$$

When a condition of equilibrium is reached we have:

$$\frac{a}{bc} = k.$$

What would be the effect of having a large quantity of ammonia present? Evidently **b** would be much larger and **c** would have to become much smaller, in order that **k** remain unchanged. But if there were very little HCl formed there must be very little ammonium chloride dissociated. The presence of a large amount of ammonia prevents the dissociation of ammonium chloride by heat.

240. Example 5. Ionization. When an acid, base, or salt is dissolved it is ionized to a greater or less extent. A definite equilibrium is established between the undissociated material and the ions, and the law of mass action holds true. Sodium chloride breaks up in solution into sodium and chlorine ions, and we have:
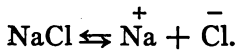
$$\text{NaCl} \leftrightarrows \overset{+}{\text{Na}} + \overset{-}{\text{Cl}}.$$
$$\text{a} \qquad\quad \text{b} \qquad \text{c}$$

$$\frac{a}{bc} = k.$$

Suppose a large quantity of hydrochloric acid be added. This acid is highly dissociated in solution and the concentration of the Cl ions will be increased. That means that the concen-

tration of the Na ions must be decreased, or, what is the same thing, the concentration of the undissociated sodium chloride must be increased.

If the solution had been saturated, some more salt would have to crystallize out to restore the equilibrium.

241. The formation of precipitates. In the case of a so-called insoluble substance surrounded by a liquid, we must recognize that some of it does go into solution, and that there is a definite equilibrium between the solid and dissolved portions. In other words, when a precipitate is formed the liquid is a saturated solution of that substance.

The undissociated dissolved substance is in equilibrium with its ions. Calling the corresponding concentrations **a, b,** and **c,** we have:

$$\frac{a}{bc} = k.$$

Since **a** is the concentration of a substance in a saturated solution, it is a constant; therefore the product of the concentrations of the ions, **bc,** in such a solution is a constant. The product of the concentrations of the ions of a substance in its **saturated solution** is known as the **solubility product** of that substance.

If a substance be added that increases the concentration of the ions, the product of these concentrations becomes greater than the solubility product, and more of the substance separates as a precipitate. If a substance be added that lessens the concentrations of the ions, more of the solid will go into solution.

For example, consider the case of barium sulphate:

$$BaSO_4 \text{ undissociated} \rightleftharpoons \overset{++}{Ba} + \overset{--}{SO_4}.$$
$$\quad a \qquad\qquad\qquad\qquad b \quad\ \ c$$
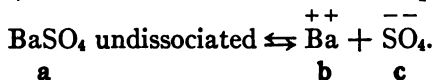
$$\frac{a}{bc} = k.$$

Since this is the case of a saturated solution, **bc** is the solubility product and is a constant.

If an excess of barium chloride be added to a solution of sodium sulphate, the solution would for an instant contain

very high concentrations of barium and sulphate ions; the product of these concentrations would be much greater than the solubility product, bc, and barium sulphate would be precipitated.

242. Precipitation of a soluble salt from solution by the addition of an excess of a reagent having a common ion. Consider the case of a saturated solution of sodium nitrate.

The dissolved salt, undissociated, is in equilibrium with its ions:

$$NaNO_3 \text{ undissociated} \leftrightarrows \overset{+}{Na} + \overset{-}{NO_3},$$
$$\qquad a \qquad\qquad\qquad b \quad\; c$$
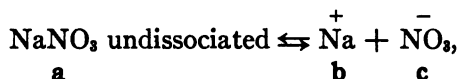
and we have:

$$\frac{a}{bc} = k.$$

Since **a** is constant, bc is a constant and equal to the solubility product of sodium nitrate.

Now suppose a large quantity of nitric acid be added to the solution. The concentration of the NO_3 ion will be increased, and, since bc is a constant, b must decrease. That means that more undissociated $NaNO_3$ must be formed. The solution, however, was already saturated; therefore salt will be precipitated.

243. Precipitation of silver acetate. Again, we might consider the case of a saturated solution of silver acetate:

$$AgC_2H_3O_2 \text{ undissociated} \leftrightarrows \overset{+}{Ag} + \overset{-}{C_2H_3O_2}.$$
$$\qquad a \qquad\qquad\qquad b \qquad\; c$$
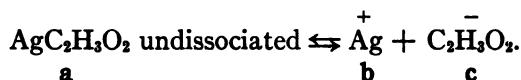
$$\frac{a}{bc} = k.$$

a is a saturated solution and therefore a constant; bc must be a constant. If silver nitrate be added, the concentration of the silver ions will increase and the concentration of the acetate ions must decrease. This would cause a precipitation of some of the salt.

244. The addition of highly dissociated acids or salts to solutions of weak acids. If a large amount of sodium acetate be added to a solution of acetic acid, the acid properties of the solution almost disappear.

Acetic acid is a weak acid; that is, it is only slightly dissociated in solution.

$$HC_2H_3O_2 \text{ undissociated} \leftrightarrows \overset{+}{H} + \overset{-}{C_2H_3O_2}.$$
$$\phantom{HC_2H_3O_2 \text{ undissociate}} a b c$$
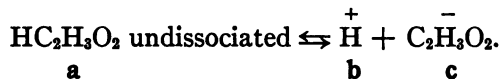
The equilibrium equation would be:

$$\frac{a}{bc} = k.$$

When the sodium acetate is added the concentration of the acetate ions becomes very much larger and therefore the concentration of the hydrogen ions must decrease. As it was already very small, the result is that almost no hydrogen ions are left in the solution, and therefore the acid nature of the solution almost disappears.

245. Addition of hydrochloric acid to a solution of acetic acid causes an almost complete suppression of the acetate ions.

$$HC_2H_3O_2 \text{ undissociated} \leftrightarrows \overset{+}{H} + \overset{-}{C_2H_3O_2}.$$
$$\phantom{HC_2H_3O_2 \text{ undissociate}} a b c$$
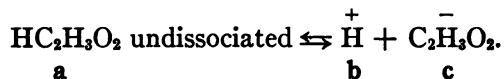
The equilibrium equation gives:

$$\frac{a}{bc} = k.$$

Hydrochloric acid is almost completely dissociated in solution; its addition therefore causes a large increase in the concentration of the hydrogen ions, with a resulting decrease in the acetate ions. As the concentration of the acetate ions was already rather small, it is reduced to almost nothing.

If hydrochloric acid be added to a solution of hydrogen sulphide, the S ions are diminished to such an extent that the solution will not blacken silver iodide paper immersed in it.

Hydrogen sulphide is a very weak acid. It is slightly dissociated in solution according to the equation:

$$H_2S \text{ undissociated} \leftrightarrows 2\overset{+}{H} + \overset{--}{S}.$$
$$\phantom{H_2S \text{ undiss}} a b c$$
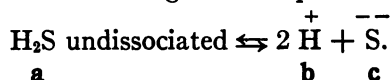
The equilibrium equation gives:

$$\frac{a}{b^2c} = k.$$

When the HCl is added the concentration b is very greatly increased and the concentration c correspondingly decreased. This means that as a result there are so few S ions that there is no chance for the formation of sulphides with salts of metals.

246. The necessity for an excess of reagent to produce complete precipitation. In many cases the solubility of the precipitate is sufficiently appreciable to prevent complete precipitation if exactly the theoretical amount of the precipitant is used.

In such cases it is necessary to use an excess of the reagent.

For example, consider the case of the precipitation of calcium oxalate. We have:

$$\overset{++}{CaC_2O_4} \text{ undissociated} \rightleftharpoons \overset{++}{Ca} + \overset{--}{C_2O_4}.$$
$$a b c$$

$$\frac{a}{bc} = k.$$
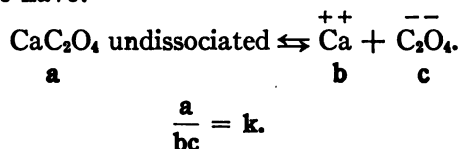
a is a constant in the saturated solution; bc is therefore a constant and equal to the solubility product of calcium oxalate.

Suppose an excess of ammonium oxalate be added; this substance, being a salt, is highly dissociated, the concentration of the oxalate ions is greatly increased, and consequently the concentration of the calcium ions must be decreased. This necessitates a precipitation of more calcium oxalate.

247. The prevention of the formation of precipitates. Why cannot zinc sulphide be precipitated in an acid solution?

Assume that hydrochloric acid is present in considerable quantity, so that the concentration of the H ions is large.

Hydrogen sulphide is very slightly dissociated.

$$H_2S \text{ undissociated} \rightleftharpoons 2\overset{+}{H} + \overset{--}{S}.$$
$$a b c$$

$$\frac{a}{b^2c} = k.$$
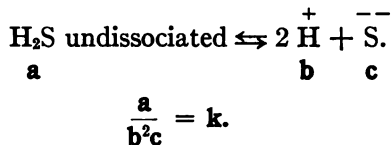
The addition of the hydrochloric acid vastly increases the concentration of the hydrogen ions and consequently decreases the concentration of the S ions.

If zinc be present in the above solution, the product of the concentration of the zinc and sulphide ions is very small and

consequently less than the solubility product of zinc sulphide. Therefore zinc sulphide will not precipitate, and if it were present it would be dissolved.

If copper were present in the solution, the product of the concentrations of the sulphur and copper ions would be greater than the solubility product of copper sulphide, and there would be a precipitation of the latter.

248. Why does calcium oxalate dissolve in hydrochloric acid? The equilibrium equation gives:

$$CaC_2O_4 \text{ undissociated} \leftrightarrows \overset{++}{Ca} + \overset{--}{C_2O_4}.$$
$$\quad a \qquad\qquad\qquad b' \quad\ c$$
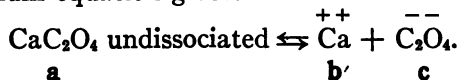
$$\frac{a}{bc} = k;$$

or, since a is a constant, bc is a constant. If hydrochloric acid be added, a large quantity of hydrogen ions are introduced into the solution, and, since oxalic acid is only slightly dissociated, the concentration of the oxalate ions will be decreased because they form undissociated oxalic acid, and more of the calcium oxalate must dissolve to make up the loss.

249. Action of ammonium chloride on magnesium hydroxide. Ammonium hydroxide produces a precipitate of magnesium hydroxide, because the product of the concentrations of the magnesium ions and the hydroxide ions is greater than the solubility product of magnesium hydroxide.

Now, if a large quantity of ammonium ions be added in the form of ammonium chloride, the concentration of the hydroxide ions of the ammonium hydroxide must decrease. In the equilibrium equation:

$$Mg(OH)_2 \text{ undissociated} \leftrightarrows \overset{++}{Mg} + 2\,\overset{-}{OH}.$$
$$\quad a \qquad\qquad\qquad b \quad\ c$$
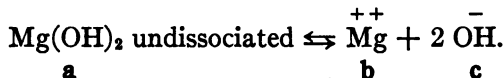
$$\frac{a}{bc^2} = k.$$

a is a constant; therefore bc must be a constant.

If the concentration of the OH be decreased, the product bc would be less than the solubility product of magnesium hydroxide. That means that there would not only be no precipitation of magnesium hydroxide but, if there were any of the

undissolved material present, it would have to go into solution to bring up the concentration b to the required point.

250. Hydrolysis. Many salts are hydrolyzed by water. That is, they react with the water to reform the acid and base from which they were originally formed. This is true of salts that are either compounds of strong acids with weak bases, strong bases with weak acids, or weak acids with weak bases.

By a strong acid or base is meant one that is highly dissociated in water solution.

For example, a water solution of potassium cyanide reacts alkaline. It is a compound of the strong base KOH with the weak acid HCN.

$$KCN + HOH \leftrightarrows KOH + HCN.$$

Since the KOH is highly dissociated in solution, it would furnish a large quantity of OH ions, and since the hydrocyanic acid is a weak acid and only slightly dissociated, it would not furnish enough hydrogen ions to neutralize the alkaline effect of the OH.

Zinc sulphate in water reacts acid. Sulphuric acid and zinc hydroxide are theoretically formed. The acid is highly dissociated and furnishes hydrogen ions. Zinc hydroxide is a weak base and prevents the formation of enough OH ions to neutralize the effect of the hydrogen ions.

Bismuth trichloride is actually dissociated into bismuth oxychloride and hydrochloric acid, according to the equation,

$$BiCl_3 + H_2O = \underline{BiOCl} + 2\ HCl,$$
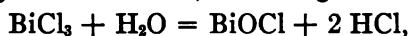
giving a precipitate of the oxychloride and forming free hydrochloric acid.

251. Exercise. Explain the reaction of the following substances with water: antimony chloride; zinc chloride; copper sulphate; aluminum sulphate; potassium sulphide; sodium carbonate; sodium phosphate.

Questions

1. What is meant by chemical equilibrium? (233).
2. What is a reversible reaction? (233).
3. Name three classes of reactions which go to virtual completion (234).
4. State the law of mass action (235).

5. State Henry's law and show how it illustrates the law of mass action (236).
6. Explain ionic equilibrium (240).
7. What is meant by the solubility product? (241).
8. Mention several slightly dissociated substances (245).
9. Why does the presence of an excess of ammonium chloride prevent the precipitation of magnesium hydroxide by ammonia? (249).
10. What is meant by hydrolysis? (250).
11. Why does ferric chloride solution in water react acid? (250).

CHAPTER XVIII

Simple Problems in Elementary Inorganic Chemistry

The problems or arithmetical examples of elementary chemistry divide themselves into five distinct classes. Each case should be taught thoroughly by itself. When the pupil has once mastered these five he will be able to solve at once almost any problem that may arise, often being able to write an expression for the result at once almost without thought.

252. **First class. Weights only. How many grams of a substance are necessary to combine with or produce a certain number of grams of another substance?**

Example. 10 g. of sodium nitrate could be formed from how many grams of nitric acid?

It is generally best to write an equation showing the possible reaction, although if the chemical equivalents are surely known this is not necessary:

$$\overset{?\ g.}{\text{NaOH}} + \underset{63}{\text{HNO}_3} = \overset{10\ g.}{\underset{85}{\text{NaNO}_3}} + \text{H}_2\text{O}.$$
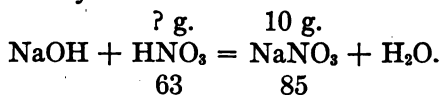
From this it appears that one molecule of nitric acid is exactly equivalent to one molecule of sodium nitrate.

That is, that 63 weights of nitric acid will form exactly 85 weights of the salt. One weight would form $\frac{1}{63}$ of 85 weights, and therefore as many weights would be necessary to form 10 as $\frac{85}{63}$ is contained in 10, or $\frac{63}{85} \times 10$.

Or it might be done by proportion, which amounts to exactly the same thing. **The unknown weight in grams is to the given weight in grams as the molecular weight of the unknown substance is to the molecular weight of the known substance.**

This would give $\dfrac{X}{10} = \dfrac{63}{85}$, or $X = \dfrac{63}{85} \times 10$.

253. Second class. Weight of a substance and volume of a gas.

(*a*) **Example.** How many liters of carbon dioxide, at normal temperature and pressure, could be formed by the use of 10 g. of sulphuric acid?

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2.$$
$$98 \qquad\qquad\qquad\qquad 44$$
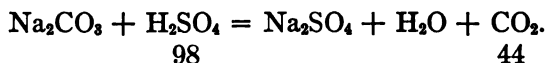
98 g., 1 gram-molecule, of sulphuric acid would form 1 gram-molecule of carbon dioxide, which would be 22.4 liters.   10 g. would form $\dfrac{10}{98}$ as much, or $\dfrac{10}{98}$ 22.4 liters.

(*b*) **Example.** 10 liters of sulphur dioxide would form how many grams of sodium sulphite?

$$SO_2 + 2NaOH = Na_2SO_3 + H_2O.$$
$$64 \qquad\qquad 126$$
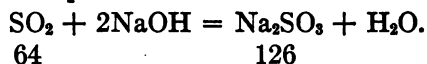
64 g. of sulphur dioxide, 1 gram-molecule, occupy 22.4 liters. 22.4 liters of this gas would therefore form 126 gr. of the salt.   10 liters would form $\dfrac{10}{22.4}$ as much, or $\dfrac{10}{22.4}$ 126 gr. of sodium sulphite.

254. Third class. Reduction of gas volumes.

Given the volume of a body of gas at a certain temperature and pressure, to find the volume corresponding to any other temperature and pressure.

Example. A volume of nitrogen is measured at a temperature of $10°$ C. and pressure of 780 mm. and found to be 10 c.c. What would be the corresponding volume at $20°$ and 790 mm.?

The volume of a body of gas varies directly as its absolute temperature. In this case the temperature has increased; therefore the volume would be increased. The absolute temperatures concerned are 283° and 293°; therefore the given volume should be multiplied by $\dfrac{293}{283}$. This will give the new volume, considering temperature alone.

The volume of a body of gas varies inversely as the pressure. The pressure in this case has increased, and the volume would

be decreased on account of the pressure change. Therefore the above new volume should be multiplied by $\dfrac{780}{790}$.

The final reduced volume would be:

$$10 \times \frac{293}{283} \times \frac{780}{790} \text{ c.c.}$$

255. Fourth class. Volumes of gases only.

Example. What volume of oxygen would be necessary to burn 10 liters of alcohol vapor? What would be the volumes of the gaseous products?

$$C_2H_6O + 3 O_2 = 3 H_2O + 2 CO_2.$$

1 vol.　　3 vols.　　3 vols.　　2 vols.
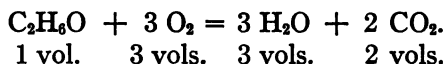
First write a molecular equation representing the reaction.

Equal volumes of all gases at the same temperature and pressure contain equal numbers of molecules.

In other words, all gaseous molecules occupy equal volumes of space. The coefficients in a molecular equation represent at once the relative combining volumes of the indicated substances in the gaseous form.

That means, in the above equation, that 1 volume of alcohol vapor would combine with 3 volumes of oxygen and form 3 volumes of water vapor and 2 volumes of carbon dioxide. Or that 10 liters of alcohol vapor would require 30 liters of oxygen to burn it, and there would be formed 30 liters of water vapor and 20 liters of carbon dioxide.

256. Fifth class. Examples involving the percentage of substance in solution and the specific gravity and volume of the liquid.

In the majority of chemical operations the reagents are handled in solution, the specific gravity of the liquid and the per cent of the substance in solution being known.

The problem is exactly like the simple case in **252** except that, in place of a definite weight being given or required, a volume of a certain solution, containing a certain per cent of material and having a given specific gravity, is given or required.

If a volume of a liquid is given, find at once the amount of available material it contains and proceed as in **252**.

If the volume of a liquid is required, first find the number

of grams required, as in **252**, and then reduce this number to the volume of the solution necessary to give it.

It may be that the volume of one liquid is given, to find the volume of another liquid concerned.

(*a*) **Example 1.   100 c.c. of sulphuric acid solution, having a specific gravity of 1.84 and containing 98 % acid, will form how many grams of hydrochloric acid?**

In all of these examples, if we call S the specific gravity of the liquid, P the per cent of substance in solution, and W the weight of material in volume V, the following expression holds true:

$$\text{SVP} = \text{W, or V} = \frac{W}{SP}, \; P = \frac{W}{SV}, \text{ and } S = \frac{W}{VP}.$$

In using these expressions never confuse volumes of gases with volumes of liquid.

100 c.c. of the acid would contain $100 \times 1.84 \times .98$ g. of H_2SO_4, which equals 180.3 g.:

$$H_2SO_4 + 2\,NaCl = Na_2SO_4 + 2\,HCl.$$
$$98 73$$
$$180.3\text{ g.} ?\text{ g.}$$
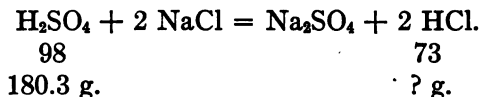
One molecule of sulphuric acid is equivalent to two molecules of hydrochloric acid. That is, 180.3 g. of sulphuric acid would produce $\frac{73}{98} \times 180.3$ g. of hydrochloric acid.

(*b*) **Example 2.   How many cubic centimeters of a barium chloride solution, having a specific gravity of 1.1 and containing 10 % barium chloride, would precipitate 2 g. of sulphuric acid?**

$$BaCl_2 + H_2SO_4 = \underline{BaSO_4} + 2\,HCl.$$
$$208 98$$
$$?\text{ g.} 2\text{ g.}$$
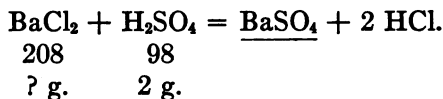
$\frac{208}{98} \times 2$ g. of barium chloride would be necessary.   This amount would be contained in as many cubic centimeters of the solution as SP (= .11) is contained in W (= $\frac{208}{98} \times 2$), or

$$\frac{208 \times 2}{98 \times .11}\text{ c.c}$$

(c) **Example 3.** How many cubic centimeters of a solution of potassium permanganate, 1 c.c. of which contains .1 g. of the salt, would be necessary to oxidize all the iron contained in 100 c.c. of a solution of ferrous sulphate having a specific gravity of 1.1 and containing 10 % of $FeSO_4$?

SVP = W. $1.1 \times 100 \times .10 = 11$ g. of $FeSO_4$ contained in the solution to be oxidized.

$$10\ FeSO_4 + 2\ KMnO_4 + 8\ H_2SO_4 = 5\ Fe_2(SO_4)_3 + K_2SO_4 + 2\ MnSO_4 + 8\ H_2O.$$

$$\begin{matrix} 1520 & 316 \\ 11\ g. & ?\ g. \end{matrix}$$

The number of grams of potassium permanganate necessary would be $\dfrac{316}{1520} \times 11$, and this would be contained in as many cubic centimeters of the solution as .1 is contained in it, or $\dfrac{316 \times 11}{1520 \times .1}$.

Example 4. How many cubic centimeters of hydrochloric acid solution, having a specific gravity of 1.2 and containing 40 % acid, would be necessary to form 100 liters of carbon dioxide?

One liter of carbon dioxide weighs $\dfrac{44}{22.4} = 1.98$ g. 100 liters would weigh 198 g.:

$$CaCO_3 + 2\ HCl = CaCl_2 + H_2O + CO_2.$$

$$\begin{matrix} & 73 & & 44 \\ & ?\ g. & & 198\ g. \end{matrix}$$
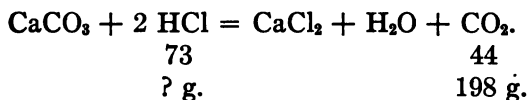
The number of grams of hydrochloric acid would be $\dfrac{73}{44} \times 198$ g.

$$V = \frac{W}{SP} = \frac{73 \times 198}{1.2 \times .40 \times 44} = \text{number of cubic centimeters of}$$

the solution.

Questions

1. What is a gram-molecule? (215). What volume does a gram-molecular weight of a gas occupy at normal temperature and pressure? (216).
2. Two gram-molecular weights of hydrochloric acid will produce how many liters of carbon dioxide? (253).

3. 12 g. of carbon will produce how many liters of carbon dioxide?
4. What relation does the specific gravity of a substance bear to the weight of a cubic centimeter in grams?
5. Given the volume and specific gravity of a solution with the percentage of substance dissolved, how do you find the weight of dissolved material contained in that volume? (256 *a*).

CHAPTER XIX

REVIEW EXERCISES

257. Necessity for reviews. In the study of any subject it is desirable to have systematic reviews on subjects or problems involving fundamental principles. This is especially true of the study of chemistry. These reviews should be instituted whenever the nature of the work admits of it, and the same ground should be gone over repeatedly. Such reviews serve to fix in the pupil's mind some of the fundamental principles so thoroughly that he is enabled to answer many questions directly from the principles involved, whether or not he has been trained on the particular questions involved.

258. Review Exercise No. 1. There are many important chemical transformations in elementary chemistry with which the student should be very familiar. Some of these are listed in **Table I.** The student should learn to state the various steps as actually carried out in practice, as well as to represent the successive changes by equations. It is safe to say that any student who can do this, as called for in Table I, is necessarily well grounded in the principles of elementary chemistry. If there are two or more methods, he should learn them all, especially the common technical method. If the laboratory or analytical method is different from the technical method, that should also be thoroughly learned.

For example, consider No. 23, Table I. How to change mercury to mercuric chloride.

Technical. Dissolve the mercury in sulphuric acid, getting mercuric sulphate. Heat the mercuric sulphate with sodium chloride, and mercuric chloride will sublime out:

$$Hg + 2\ H_2SO_4 = HgSO_4 + SO_2 + 2\ H_2O.$$
$$HgSO_4 + 2\ NaCl = HgCl_2 + Na_2SO_4.$$
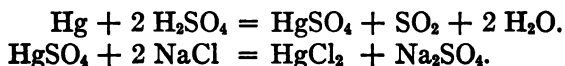
Laboratory method.   Dissolve the mercury in aqua regia:

$$2 \, HNO_3 = \; H_2O \; + 2 \, NO + 3 \, O.$$
$$3 \, O + 6 \, HCl = 3 \, H_2O + 3 \, Cl_2.$$
$$3 \, Hg + \; 3 \, Cl_2 \; = 3 \, HgCl_2.$$
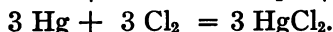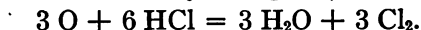
Adding these equations, we have:

$$3 \, Hg + 2 \, HNO_3 + 6 \, HCl = 3 \, HgCl_2 + 4 \, H_2O + 2 \, NO.$$
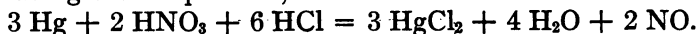
The student is not expected to invent any of the reactions; he is expected to look up the actual methods in the text-book.   All reactions represented must be possible.

TABLE I

259. Review Exercise No. 1.   Indicate by equations the following transformations:

1. Sodium to sodium chloride (76).
2. Calcium oxide to calcium nitrate (78).
3. Aluminum sulphate to aluminum hydroxide (85).
4. Sodium chloride to sodium sulphate (82).
5. Aluminum hydroxide to aluminum sulphate (80).
6. Calcium carbonate to calcium chloride (82).
7. Sodium sulphate to sodium chloride (85).
8. Sulphur trioxide to sodium sulphate (93).
9. Sodium chloride to sodium (626).
10. Calcium to calcium nitrate (140).
11. Calcium chloride to calcium nitrate (82, 85).
12. Barium nitrate to barium chloride (82, 85).
13. Cupric sulphate to cupric oxide (751).
14. Mercuric oxide to mercury (737).
15. Mercuric chloride to mercuric oxide (737).
16. Barium sulphate to barium chloride (692).
17. Strontium chloride to strontium oxide (85).
18. Silver to silver chloride (85, 140).
19. Copper to cupric sulphate (138).
20. Copper to cupric chloride (268).
21. Cupric chloride to cuprous chloride (750).
22. Silver chloride to silver nitrate (196).
23. Mercury to mercuric chloride (268).
24. Mercury to mercurous chloride (735–736).

25. Stannous chloride to stannic chloride (143).
26. Ferrous chloride to ferric chloride (143).
27. Cuprous chloride to cupric chloride (143).
28. Ferrous sulphate to ferric sulphate (144).
29. Ferrous chloride to ferric sulphate (145).
30. Mercurous chloride to mercuric sulphate (145).
31. Stannous chloride to stannic sulphate (145).
32. Sulphur to hydrogen sulphide (398).
33. Sulphuric acid to sulphur dioxide (138).
34. Nitric acid to ammonia (459).
35. Sodium hydroxide to sodium aluminate (802).
36. Chromous oxide to chromic acid (136).
37. Potassium dichromate to potassium chromate (819).
38. Iodine to iodic acid (135).
39. Potassium dichromate to chromic chloride (129).
40. Manganese dioxide to permanganic acid (136).

260. Review Exercise No. 2. With the intention of fixing in the student's mind the natural forms in which the common elements occur, as well as the processes by which they are transformed to the common artificial compounds, the following exercise has been designed:

Table II gives some of the natural sources of the common elements and **Table III** gives the names of many common elements and compounds.

The student is assigned some element or compound from **Table III**, by number, and he is expected to start with natural elements or compounds from **Table I** and state in words what operations are necessary to produce the given substance. He is not allowed to make use of any substance whose formation from the natural substances he has not first shown. He can best represent all changes by equations, and then in his recitation translate his equations into words.

The value of this exercise cannot be overestimated. It results in fixing in the mind the relative importance of certain artificial compounds and fundamental processes in a way that no ordinary laboratory or text-book work can do.

261. Example. Required, to show the formation of ferrous

sulphate from the natural elements or compounds. The raw
materials are: sulphur, oxygen, water, ferric oxide, carbon.

$$S + O_2 = SO_2. \qquad\qquad C + O_2 = CO_2.$$
$$2\,SO_2 + O_2 = 2\,SO_3. \qquad\qquad CO_2 + C = 2\,CO.$$
$$SO_3 + H_2O = H_2SO_4. \qquad Fe_2O_3 + 3\,CO = 2\,Fe + 3\,CO_2.$$
$$Fe + dil.\ H_2SO_4 = FeSO_4 + H_2.$$
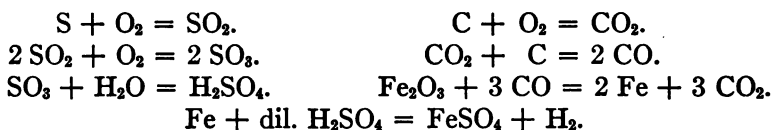
262. Example. Required to show the formation of zinc sul-
phate from the natural elements or compounds:

$$S + O_2 = SO_2. \qquad\qquad ZnCO_3 = ZnO + CO_2.$$
$$2\,SO_2 + O_2 = 2\,SO_3. \qquad\qquad ZnO + C = Zn + CO.$$
$$SO_3 + H_2O = H_2SO_4. \qquad Zn + H_2SO_4 = ZnSO_4 + H_2.$$

TABLE II

**263. Table of natural elements and compounds from which nearly
all other common compounds and elements may be made.**

First Group

Sodium chloride.
Sodium nitrate.
Potassium chloride.

Second Group

Magnesium carbonate.
Magnesium sulphate.
Calcium carbonate.
Calcium sulphate.
Strontium carbonate.
Strontium sulphate.
Barium carbonate.
Barium sulphate.
Zinc carbonate.
Zinc sulphide.
Cadmium sulphide.
Mercury.
Mercury sulphide.

Third Group

Aluminum sulphate.
Aluminum silicate.
Borax, $Na_2B_4O_7$.

Fourth Group

Carbon.
Carbon dioxide.
Calcium carbonate.
Silicon dioxide.
Aluminum silicate.
Tin dioxide.
Lead sulphide.

Fifth Group

Nitrogen.
Sodium nitrate.
Calcium phosphate.
Arsenic.

Arsenic sulphide.
Antimony sulphide.
Bismuth sulphide.

Potassium chloride.
Sodium bromide.
Potassium iodate.
Manganese dioxide.

Sixth Group

Oxygen.
Hydrogen oxide.
Sulphur.
Calcium sulphate.
Sulphides.
Iron pyrite.

Eighth Group

Ferrous carbonate.
Ferric oxide.
Nickelous carbonate.
Copper carbonate.
Copper.
Silver.
Silver sulphide.
Silver chloride.
Gold.
Platinum.

Seventh Group

Calcium fluoride.
Sodium chloride.

TABLE III

264. Common artificial compounds. Indicate by equations the formation of each of the following compounds or elements from the natural elements or compounds, as given in a previous table. Use no reagents whose formation from natural substances you have not shown.

1. Sulphuric acid.
2. Hydrochloric acid.
3. Nitric acid.
4. Calcium oxide.
5. Carbon dioxide.
6. Calcium hydroxide.
7. Sodium hydroxide.
8. Sodium carbonate.
9. Sodium bicarbonate.
10. Ammonia.
11. Hydrogen sulphide.
12. Cupric oxide.
13. Cuprous oxide.
14. Cupric sulphate.
15. Ferrous chloride.
16. Ferric hydroxide.
17. Ferrous sulphate.
18. Hydrogen.
19. Iodine.
20. Bromine.
21. Aluminum   bromide.
22. Ammonium   acetate.
23. Cadmium   chlorate.
24. Calcium   hydroxide.
25. Cupric   nitrate.
26. Cuprous   carbonate.
27. Magnesium   sulphide.
28. Nickelous   sulphate.

29. Potassium   phosphate.
30. Sodium   oxide.
31. Lead   nitrite.
32. Barium   sulphite.
33. Zinc   chloride.
34. Acetic acid.
35. Arsenic acid.
36. Boric acid.
37. Hydrobromic acid.
38. Hydriodic acid.
39. Hydrofluoric acid.
40. Phosphoric acid.
41. Antimony.
42. Barium.
43. Copper.
44. Tin.
45. Lead.
46. Manganese.
47. Mercury.
48. Silver.
49. Iron.
50. Zinc.
51. Aluminum.
52. Ammonium chloride.
53. Ammonium arsenate.
54. Antimony sulphide.

55. Barium chromate.
56. Chromic sulphate.
57. Hydrogen.
58. Hydrogen peroxide.
59. Iodic acid.
60. Lead chromate.
61. Manganous sulphate.
62. Mercuric chloride.
63. Mercurous chloride.
64. Mercuric oxide.
65. Mercurous oxide.
66. Mercuric nitrate.
67. Mercurous nitrate.
68. Phosphorus.
69. Potassium arsenate.
70. Potassium dichromate.
71. Potassium bicarbonate.
72. Potassium chromate.
73. Potassium permanganate.
74. Silver nitrate.
75. Silver chloride.
76. Sodium arsenate.
77. Sodium thiosulphate.
78. Stannous sulphide.
79. Stannous chloride.
80. Stannic chloride.

Review Exercise No. 3

Important Questions Relating to the Fundamental Ideas of Elementary Chemistry Which Every Pupil Should Be Able to Answer Correctly at the End of Four Months of Study

The numbers following the questions refer to the paragraph in which the answer will be found.

265. Lesson I.

1. **Give the symbols and names of the common elements in groups (4).**
2. Name and give examples of each of the four kinds of chemical change (20).
3. What is catalysis? a catalytic agent? (22).

4. Give the full meaning of a symbol of an element (29).

5. Define the term "formula of a compound" (30).

6. Give the full meaning of the formula of a compound (32).

7. What is meant by valence or combining power? (40).

8. How do you know what the formula of a compound of two elements will be? (41).

9. Give the formulas and names of all of the compounds of the metals with the non-metals (41).

10. How many grams of any one element would be chemically equivalent to 10 g. of any other element? (45).

11. Define the term "chemical equation" (48).

12. Write equations showing the formation of binary compounds from the elements (50).

13. State the full meaning of an equation, making use of any equation whatever (51).

14. How many grams of a binary compound may be made from 10 g. of one of the elements? (52).

15. How many grams of any element are necessary to form 10 g. of a binary compound? (52).

16. Give the symbols and names of the radicals in groups (61).

17. Give the formulas and names of the compounds of each of the basic radicals with each of the acid radicals (62).

18. What is an acid?   Give the formulas and names of ten (63).

19. What is a base?   Give the formulas and names of ten (64).

20. What is a salt?   Give the formulas and names of ten (66).

266. Lesson II.

1. What is an alkali?   Give the formulas and names of three (65).

2. What is a basic oxide?   Give the names and formulas of ten (67).

3. What is an acidic oxide?   Give the formulas and names of ten (69).

4. What is an acid anhydride? Give the formulas and names of five (70).

5. State seven general methods for the preparation of salts and tell what else is formed in each case (76, 78, 80, 82, 85, 91, 93).

6. State the solubility rule (87).

7. Name the oxides of the common elements in groups, stating which react acid, which basic, and which may react either acidic or basic (96–103).

8. Define the term oxidation (107).

9. What is an oxidizing agent? (108).

10. Name ten oxidizing agents suitable for use in solution giving equations indicating the oxidizing power (127).

11. Write an equation showing the oxidation of phosphorus by the action of nitric acid (135).

12. How is the oxidizing power of an oxidizing agent predicted? (118).

13. Write equations indicating the liberation of the halogens from their salts by oxidizing agents in the presence of acids (130).

14. Write equations showing the oxidation of the non-metals to the corresponding acids by the use of oxidizing agents in the presence of water (**132**).

15. Write equations showing the oxidizing action of boiling concentrated sulphuric acid upon the metals (**138**).

16. Write equations showing the action of dilute nitric acid upon the metals (**140**).

17. Write equations showing the complete oxidation of organic compounds to carbon dioxide and water by the use of some oxidizing agent in the presence of sulphuric acid (**142**).

18. What is meant by reduction?   What is a reducing agent? (**148**).

19. Give the formulas of ten reducing agents suitable for use in the "dry way" (**151**).

20. Write equations indicating the reduction of the metallic oxides to the metals by the use of the agents just mentioned (**150**).

Review Exercise No. 4

Important Questions Relating to the More Advanced Theory

267. Lesson I.

1. Describe the motions of a molecule of a gas (**154**).
2. State Boyle's law (**155**).
3. How does the volume of a body of gas vary with the temperature? (**156**).
4. State Charles's law (**157**).
5. What is meant by the terms normal temperature and pressure? (**160**).
6. How long does a substance continue to dissolve? (**166**).
7. What is meant by water of crystallization? (**174**).
8. What is osmotic pressure? (**177**).
9. What is osmotic pressure analogous to? (**179**).
10. Knowing the quantity of undissociated material in solution in a given volume of water, how is it possible to tell the osmotic pressure? (**181**).
11. State the laws of osmotic pressure (**180**).
12. State the boiling-point law (**185**).
13. State the freezing-point law (**186**).
14. What is meant by dissociation as distinguished from decomposition? (**188**).
15. What is meant by electrolytic dissociation? (**191**).
16. What is an ion? an electrolyte? (**191**).
17. Name ten common substances that are highly dissociated in solution (**193**).
18. Name ten common substances that are slightly dissociated in solution (**193**).
19. What is meant by the order of activity of the metals? (**194**).

20. What is meant by the solution pressure of a metal? (194).

21. Give the names of the metals in the order of their activity (197).

268. Lesson II.

1. What classes of solutions will conduct the electric current? (201).

2. State Faraday's law (205).

3. What is specific heat? (206).

4. State the law of DuLong and Petit (208).

5. What is heat of formation and heat of decomposition? (209).

6. How is it possible to estimate the heat of reaction? (210).

7. What is an endothermic reaction? an exothermic reaction? (209).

8. State Gay Lussac's law of combining volumes (212).

9. What is a gram-molecule? (213).

10. What is the gram-molecular volume? (216).

11. How is the molecular weight of a gas determined? (217).

12. How is the molecular weight of a solid which cannot be converted to a gas determined? (219).

13. What is meant by the terms gas and vapor densities? (220).

14. How is the correct formula of a substance determined from its analysis and molecular weight? (223).

15. How is the atomic weight of an element forming a series of gaseous compounds determined? (226).

16. If an element does not form gaseous compounds, how may its atomic weight be determined? (228).

17. How are accurate atomic weights determined? (227).

18. What is meant by chemical equilibrium? (233).

19. What is a reversible reaction? (233).

20. Name three classes of reaction which go to virtual completion (234).

269. Lesson III.

1. State the law of mass action (235).

2. State Henry's law and show how it illustrates the law of mass action (236).

3. Explain ionic equilibrium (240).

4. What is meant by the solubility product? (241).

5. Why does ferric chloride solution in water react acid? (250).

6. What is hydrolysis? (250).

Review Exercise No. 5

Questions from College Examination Papers

270. Lesson I.

1. Describe two modifications of oxygen and state how they may be prepared (296–307).

2. Mention five substances that give up oxygen when heated (300).

3. How may hydrogen peroxide be prepared? And describe some of its properties (342).

4. Describe a test for ozone which distinguishes it from bromine or chlorine (307).

5. How could you recognize the products that are formed when sulphur, carbon, iron, phosphorus, and hydrogen are burned in oxygen?

6. Describe your laboratory method for the preparation of hydrogen and mention all precautions necessary (322).

7. How may oxygen and nitrogen be caused to combine? (463).

8. How could you prove that the manganese dioxide undergoes no change when used with potassium chlorate in the preparation of oxygen?

9. What are the constituents of the atmosphere? Give the approximate proportions of the four most abundant constituents (434).

10. What oxides does nitrogen form and which of these are anhydrides? (419).

11. State the exact meaning of the symbols H; S; Fe (29).

12. State the exact meaning of the formulas H_2; S_8; H_2SO_4 (29, 32).

13. State the full meaning of the equation $Zn + H_2SO_4 = ZnSO_4 + H_2$ (51).

14. State seven general methods for the preparation of salts (76, 78, 80, 82, 85, 91).

15. Write equations showing the formation of sodium sulphate in six different ways (76–91).

16. What is a dibasic acid? a diacid base? a basic salt? an acid salt? (Lab. Ex. No. 28).

17. How many liters of oxygen will 13 g. of mercuric oxide yield? (253).

18. How many grams of sulphuric acid would be necessary to form 10 liters of hydrogen? (253).

19. What are the halogens? Describe each briefly (Chap. XXVI).

20. What kind of a chemical agent is required to free chlorine from hydrochloric acid? (128).

21. Explain under what conditions, if any, hydrochloric acid acts upon the following substances and what is formed in each case: sodium hydroxide, zinc oxide, zinc, iron sulphide, sodium carbonate, barium dioxide, manganese dioxide. Write all equations.

22. What is the test for the chlorine radical? (353).

23. How could you change sulphur into hydrogen sulphide? (398).

271. Lesson II.

1. How did you make sulphuric acid and how did you recognize the product?

2. Under what condition, if any, does sulphuric acid act upon the following substances: copper, lead, iron, carbon, sulphur, sodium carbonate, barium dioxide, calcium fluoride, sodium chloride?

3. State two general methods for the preparation of the halogen acids (354–376).

4. Explain the use of hydrogen sulphide in the separation of copper and zinc (399).

5. How did you make sodium sulphite from sulphur?

6. State exactly what takes place when sodium hydroxide is neutralized with hydrochloric acid (80).

7. What is the effect of mixing hydrogen sulphide water and nitric acid? (133).

8. Describe the changes that sulphur undergoes when slowly heated (387).

9. State three different methods for the preparation of sulphur dioxide (404).

10. How would you change sodium sulphate to sodium chloride? (85).

11. State two methods for the preparation of nitrogen (421, 1–3).

12. Give the equation for the action of ammonium hydroxide on hydrochloric acid (80).

13. What would be the effect of heating ammonium chloride very hot? (429).

14. What is the action of sulphuric acid on ammonium hydroxide? (80).

15. How did you make ammonium nitrate and how did you tell when it was sufficiently evaporated?

16. What actually happens when ammonium chloride is heated? (429).

17. How may ammonia be obtained from an ammonium compound? (429).

18. What is the effect of heating a mixture of ammonium sulphate and common salt? (658).

19. How did you make nitric acid and what is its chief characteristic? (461).

20. Write the equations showing the action of nitric acid on copper (140).

272. Lesson III.

1. If copper scale is dissolved in dilute nitric acid, what compound would be formed?

2. Suppose sodium hydroxide were added to this solution, and the solution heated, what would be the precipitate? (751).

3. Suppose copper scale were dissolved in dilute hydrochloric acid, what compound would be formed?

4. If sodium hydroxide were added to this solution and the solution heated, how would this precipitate compare with the last? (750).

5. What is aqua regia?   Represent its action by equations.

6. What is the action of strong nitric acid on zinc? (140).

7. What is the action of very dilute nitric acid on zinc?   Give equations (459).

8. What is the action of an excess of strong nitric acid on yellow ammonium sulphide? (133).

9. How may red phosphorus be changed to yellow and yellow to red?

10. What is the effect of adding bromine water to red phosphorus? (135).

11. What is the effect of adding iodine water to red phosphorus? (135).

12. What is the effect of dissolving red phosphorus in nitric acid, adding silver nitrate and ammonia so as not to mix? (135).

13. Describe the effect of heating arsenic in closed tube (478).

14. Describe the effect of heating arsenic in air (479).

15. What is the effect of heating arsenious oxide with charcoal? (481).

16. What is the effect of heating arsenious oxide in closed tube? (484).

17. What effect has bromine water on metallic arsenic? (132 a).

18. What is the color of silver arsenate?

19. What is formed when arsenic is dissolved in concentrated nitric acid? (132 a).

20. What is the reaction between ammonium hydroxide and arsenic trioxide? (91). What is the color of silver arsenite?

21. Which is the more soluble, arsenious oxide or arsenic oxide?

22. What is formed when bromine water acts on arsenious oxide? (136).

23. What is the action of concentrated nitric acid on powdered antimony? (132 a).

273. Lesson IV.

1. What is formed when bismuth carbonate is dissolved in hydrochloric acid? (82).

2. When this solution is poured into an excess of water, what is the precipitate? (250).

3. What are the three allotropic forms of carbon and what are your reasons for believing them to be the same substance? (500).

4. What is the effect of heating copper scale with charcoal? (150).

5. What is the effect of passing illuminating gas over hot cupric oxide? (150).

6. What effects are produced by passing an excess of carbon dioxide into lime-water? (678).

7. What is the effect of heating hydrogen sodium carbonate? (637).

8. What acid does carbon dioxide form with water? (515).

9. Explain the action of a water solution of sodium carbonate on litmus (250).

10. What is common baking-powder? (531).

11. What is the effect of heating Rochelle salt until all carbon is burned?

12. How did you make ortho-silicic acid? (Lab. Ex. No. 29).

13. Mention three ways of dissolving sand (554).

14. How did you make stannous chloride? (76).

15. How would you change stannous chloride into stannic chloride? (143).

16. What is the action of stannous chloride upon mercuric chloride? (Lab. Ex. No. 30).

17. What is the action of hydrogen sulphide upon stannous chloride? upon stannic chloride?

18. How do the common acids affect lead? (600).

19. What is the action of a soluble sulphate upon a solution of a lead salt? (85).

20. What is the effect of trying to dissolve red lead in dilute nitric acid? What is supposed to be the composition of red lead? (613–614).

21. What is the Solvay or ammonia process of making sodium carbonate? (634).

22. How could you distinguish between carbonate and bicarbonate of soda? (637).

23. Describe how you made sodium hydroxide in the laboratory (Lab. Ex. No. 32).

274. Lesson V.

1. What is the effect of adding concentrated hydrochloric to a saturated solution of common salt? (244).

2. What effect has silver nitrate upon a solution of potassium chlorate?

3. Describe methods for making the following salts: sodium sulphate from sodium chloride, sodium chloride from sodium sulphate, sodium acetate from sodium chloride, sodium chloride from hydrogen disodium phosphate.

4. What oxides does copper form? Describe each (749–751).

5. Describe the action of the common acids on copper, both hot and cold. Give equations where there is any action (741–742).

6. How could you change cupric chloride to cuprous chloride? (152).

7. How could you change cuprous chloride to cupric chloride? (143).

8. What is the effect of adding potassium iodide to copper sulphate solution?

9. Describe all changes when sodium hydroxide is added to a solution of cupric sulphate and the mixture heated to boiling (751).

10. State two methods for making cuprous oxide (749).

11. What is the effect of adding a piece of iron wire to a copper sulphate solution? (196).

12. How did you obtain pure silver from a silver coin?

13. How could you obtain silver nitrate from silver chloride? (196).

14. How can the precipitation of magnesium hydroxide by ammonia be prevented without making the solution acid? (249).

15. Describe lime, slaked lime, lime-water, calcium hydroxide, air-slaked lime (669).

16. How could you distinguish air-slaked lime from dry-slaked lime?

17. What is the difference between chloride of lime and calcium chloride? State the uses of each (671–673).

18. What is the formula of gypsum? What is plaster of Paris? (680).

19. Why does plaster of Paris "set"? (680).

20. Describe barium hydroxide. What happens when a solution of barium hydroxide is left exposed to the air? (691).

21. What is the action of zinc on potassium hydroxide solution? (714).

275. Lesson VI.

1. What is formed when potassium hydroxide is added to a zinc sulphate solution? (712).

2. What is the action of zinc chloride on litmus? Explain the result (250).

3. What is the action of cold and hot nitric acid on mercury? (727).

4. What is the effect of adding a sodium hydroxide solution to a solution of mercuric nitrate? (737).

5. What is the effect of adding a soluble chloride to a mercurous solution? (735).

6. What is the effect of adding sodium hydroxide to a solution of a mercuric salt? (737).

7. What is the action of the common acids on aluminum? (802).

8. What is the residue after heating aluminum chloride very hot?

9. What peculiar property has aluminum amalgam?

10. Describe chromic hydroxide (814).

11. How could you change chromic sulphate to a chromate?

12. How could you change chromium in potassium dichromate to chromic sulphate? (130).

13. What would be the effect of chromic anhydride on hydrochloric acid? (128).

14. What is the effect of adding oxalic acid to potassium permanganate solution in the presence of sulphuric acid? (142).

15. Describe the effects of the common acids on iron (790).

16. Describe ferrous hydroxide.

17. How did you change ferrous sulphate to ferric sulphate? (144).

18. Describe ferric hydroxide (790).

19. How would you change ferric hydroxide to ferric chloride and this to ferrous chloride?

20. Describe the effect of adding hydrogen sulphide to both ferrous and ferric salts in solution.

21. How did you make ferrous ammonium sulphate? (798).

22. How could you change potassium ferrocyanide to ferric chloride?

23. Why does not ammonium hydroxide give a precipitate of ferric hydroxide in a solution of potassium ferrocyanide?

24. How could you make ethyl acetate? (Lab. Ex. No. 42).

276. Lesson VII.

1. What is the general formula of an alum, and how could you make ammonium aluminum alum? (812).

2. Explain why the same amounts of heat are generated when equivalent amounts of different acids are neutralized with bases (210).

3. Describe the properties and preparation of the two chlorides of mercury (**735–736**).

4. What action, if any, has dry ammonia gas on litmus paper?

5. How is the aluminum ion detected? (**803**).

6. Describe several different tests for ferrous and ferric ions (**793**).

7. What acids does phosphorus form? (**470**).

8. How could you make lead chloride, and what remarkable property has this salt? (**600**).

9. How much methyl alcohol should be dissolved in 1 liter of water to give the same osmotic pressure that 5 g. of ethyl alcohol give when dissolved in the same volume of the same solvent? (**180**).

10. What is meant by the term "weak acid" or "weak base"? (**250**).

11. What is the method for finding the atomic weight of an element like calcium that does not form gaseous compounds? (**228**).

12. State two methods for making aluminum chloride from alum.

13. Explain the fact that the gas density of sulphuric acid is 24.5.

14. Describe and explain what takes place when a piece of zinc is placed in a solution of a lead salt (**196**).

15. Examples involving weights only (**252**).

16. Examples involving weights and volumes of gases (**253**).

17. Examples involving volumes of gases only (**255**).

18. Examples involving volumes of liquids having a certain specific gravity and a certain per cent of material in solution (**256**).

19. Derivation of formulas from analysis and vapor density (**223**).

20. General theory. See questions with references (**265, 266, 267, 268, 269**).

CHAPTER XX

TABLES

277. Solubility rules. From an inspection of Table No. V, it appears that the following rules apply to most of the common substances of the laboratory:

(1) **All the hydrogen, sodium, potassium, and ammonium compounds are soluble; also all the chlorates, acetates, and nitrates.**

(2) **All the chlorides are soluble except those of silver, lead, and mercurous mercury.**

(3) **All the sulphates are soluble except those of barium, strontium, and lead.**

(4) **All the carbonates, phosphates, silicates, and sulphides are insoluble except those of sodium, potassium, and ammonium.**

(5) **All the hydroxides are insoluble except those of sodium, potassium, ammonium, calcium, strontium, and barium.**

278. Tension of aqueous vapor. When a gas is collected over water, and the level of the water made the same outside as inside the apparatus, the pressure inside is the same as the atmospheric pressure. The pressure inside, however, is made up of two partial pressures: that due to the expansive force of the gas and that due to the expansive force of the aqueous vapor mixed with the gas. The actual pressure to which the gas is subjected is therefore equal to the difference between the atmospheric pressure and the tension of the aqueous vapor at that temperature.

TABLE NO. IV

279. Tensions of aqueous vapor, expressed in millimeters of mercury for different temperatures.

Temp.	Tension	Temp.	Tension	Temp.	Tension
0° C.	4.6				
1	4.9	11° C.	9.8	21° C.	18.5
2	5.3	12	10.4	22	19.7
3	5.7	13	11.1	23	20.9
4	6.1	14	11.9	24	22.2
5	6.5	15	12.7	25	23.6
6	7.0	16	13.5	26	25.0
7	7.5	17	14.4	27	26.5
8	8.0	18	15.4	28	28.1
9	8.5	19	16.3	29	29.8
10	9.1	20	17.4	30	31.6

TABLE V

280. Showing the solubility of some compounds in water. The numerator shows the number of parts soluble in 100 parts of water at 100° C., the denominator the number of parts soluble in 100 parts of water at 20° C.

	Bromide	Carbonate	Chloride	Chromate	Cyanide	Ferrocyanide	Ferricyanide	Hydroxide	Iodide	Nitrate	Oxide	Phosphate	Sulphate	Sulphide
Al.....	S	...	S	...	...	...	...	I	...	S	I	I	89.1*/36.1	...
NH₄...	S	S	77.3/37.2	S	S	S	S	S	S	Dec./185	...	s	103.3/75.4	S
Ba.....	149/104	I	72/42	I	S	S	S	50*/5	S	34.2/8.6	90+/3.4	I	...	Dec./Dec.
Ca.....	S	I	S	S/.4	Dec.	S	S	.066/.15	435+/204	S	Dec.	I	.21/.24	.27/.23
Cu'....	I	...	I	...	I	I	I	I	I	...	I	...	...	...
Cu''....	S	...	S	...	I	I	I	I	Dec.	S	·I	I	203/42	I
Fe''....	S	I	s/s	...	...	I	I	I	S	S	I	I	42/24	I
Fe'''...	S	...	S	...	...	I	S	I	...	S	I	I	S	I
Pb.....	s/s	I	5±/.97	I	s/s	I	s/s	I	.14/.04	7/52	I	I	I	I
Mg....	S	I	S	S	...	S	S	I	S	·S	·I	I	73/36	Dec.
Hg'....	I	...	I	s/s	...	...	...	I	I	Dec.	I	Dec./I	.3/.2	I
Hg''....	4/.4	...	54/7	Dec.	40/10	...	...	I	I	S	I	s/I	Dec.	I
K......	102/64	147+/112	56/35	79/62	S	100±/35±	77/50±	S	209/144	247/31	Dec.	S	26/11	S
Ag.....	I	I	I	I	I	I	I	I	I	1500±/227	I	I	1/.5	I
Na.....	120/88	45*/21	40/36	S	S	90±/30±	66/20	S	312/178	168/90	Dec.	S	412†/140	S
Sr	200±/99	I	102*/54	S	Dec./S	S	S	18/.88	370/179	101/71	2/.6	I	I	Dec.
Sn''....	S	I	S	...	...	I	...	I	s/s	...	I	I	Dec.	I
Zn.....	S	I	S	...	I	I	...	I	S	S	I	I	653/161	I

* Anhydrous.   s Slightly soluble.   I Insoluble.
S Very soluble.   † At 34° C.   Dec. Decomposed by boiling.

TABLE VI

281. Giving atomic weights, molecular formulas, state, melting-points, boiling-points, specific heats, and specific gravities of the elements.

Elements	Sym.	Atomic Weights	Molecular Formula	State	Melting-Point °C.	Boiling-Point °C.	Specific Heat	Specific Gravity
Aluminum...	Al	27.1	....	Solid Met.	657	1600	.214	2.68
Antimony....	Sb	120.2	....	Sol. Met.	630	1600	.0508	6.72
Argon.......	A	39.9	A	Gas. Non-met.	−187.9	−186.1	....	....
Arsenic......	As	75.0	As₄-As₂	Sol. Met.	185	449.5	.0814	4.7-5.7
Barium......	Ba	137.4	....	Sol. Met.	850	950	....	3.6
Bismuth.....	Bi	208.5	....	Sol. Met.	269	1435	.0308	9.9
Boron.......	B	11.0	....	Sol. Met.	....	....	.366	2.63
Bromine.....	Br	79.96	Br₂	Liq.Non-met.	−7.3	63.05	.0843*	3.18
Cadmium....	Cd	112.4	Cd	Sol. Met.	321.7	778	.0567	8.6
Cæsium......	Cs	132.9	....	Sol. Met.	26.37	670	....	1.85
Calcium.....	Ca	40.1	....	Sol. Met.	795	....	.170	1.55
Carbon......	C	12.00	....	Sol. Non-met.	3500	....	.459†	3.5†
Cerium......	Ce	140.25	....	Sol. Met.	623	....	.0448	....
Chlorine.....	Cl	35.45	Cl₂	Gas. Non-met.	−102	−33.6	....	....
Chromium...	Cr	52.1	....	Sol. Met.	1515	....	.100	6.92
Cobalt......	Co	59.0	....	Sol. Met.	1530	....	.107	8.5
Columbium..	Cb	94.0	....	Sol. Met.	1950	....	....	....
Copper......	Cu	63.6	....	Sol. Met.	1065	2100	.0952	8.7
Erbium......	Er	166.0	....	Sol. Met.	....	....	....	....
Fluorine.....	F	19.0	F₂	Gas. Non-met.	−223	−187	....	....
Gadolinium..	Gd	156.0	....	Sol. Met.	....	....	....	....
Gallium.....	Ga	70.0	....	Sol. Met.	30.15	....	.079	5.9
Germanium..	Ge	72.5	....	Sol. Met.	900	1350	....	5.47
Glucinum....	Gl	9.1	....	Sol. Met.	960	....	.058	1.8
Gold........	Au	197.2	....	Sol. Met.	1065	....	.0324	19.3
Helium......	He	4.0	He	Gas. Non-met.	−271.0	−267	....	....
Hydrogen....	H	1.0075	H₂	Gas. Non-met.	−256.5	−252.5	....	....
Indium......	In	115.0	....	Sol. Met.	176.0	....	.0570	7.42
Iodine.......	I	126.97	I₂-I	Sol. Non-met.	114.2	184.35	.0541	4.95
Iridium......	Ir	193.0	....	Sol. Met.	1950	....	.0326	22.38
Iron.........	Fe	55.9	....	Sol. Met.	1804	....	.114	7.78
Krypton.....	Kr	81.8	Kr	Gas. Non-met.	−169.0	−151.7	....	....
Lanthanum..	La	138.9	....	Sol. Met.	810.0	....	.0449	6.16
Lead........	Pb	206.9	....	Sol. Met.	327	1500	.0314	11.37
Lithium.....	Li	7.03	....	Sol. Met.	186	1400	.941	.59
Magnesium..	Mg	24.36	....	Sol. Met.	632	1100	.250	1.74
Manganese...	Mn	55.00	....	Sol. Met.	1245	....	.122	8
Mercury.....	Hg	200.0	Hg	Liq. Met.	−39.5	357	.0319*	13.60
Molybdenum	Mo	96.0	....	Sol. Met.	1780	....	.0722	....
Neodymium..	Nd	143.6	....	Sol. Met.	840	....	....	....
Neon.......	Ne	20.0	Ne	Gas. Non-met.	....	....	....	....
Nickel.......	Ni	58.7	....	Sol. Met.	1484	....	.108	8.57
Niton.......	Nt	222.4	....	Gas.	....	....	....	....

* Solid.   † Diamond.

TABLE VI—CONTINUED

Elements	Sym.	Atomic Weights	Molecular Formula	State	Melting-Point °C.	Boiling-Point °C.	Specific Heat	Specific Gravity
Nitrogen.....	N	14.04	N₂	Gas. Non-met.	−210.5	−196.1	....	....
Osmium.....	Os	191.0	....	Sol. Met.	2500	....	.0311	22.4
Oxygen......	O	16.0	O₂	Gas. Non-met.	−230	−184	....	....
Palladium....	Pd	106.5	....	Sol. Met.	1586	....	.0593	11.9
Phosphorus..	P	31.0	P₄	Sol. Non-met.	44.2	287.3	.189*	1.83
Platinum....	Pt	194.8	....	Sol. Met.	1775	....	.0324	21.45
Potassium...	K	39.15	....	Sol. Met.	62.5	757.5	.166	.87
Praseodimium	Pr	140.5	....	Sol. Met.	....	....	....	....
Radium.....	Ra	225.0	....	Sol. Met.	....	....	....	....
Rhodium....	Rh	103.0	....	Sol. Met.	2000	....	.0580	12.1
Rubidium....	Rb	85.5	....	Sol. Met.	38.5	....	....	1.52
Ruthenium...	Ru	101.7	....	Sol. Met.	2000	....	.0611	12.26
Samarium....	Sm	150.3	....	Sol. Met.	....	....	....	....
Scandium....	Sc	44.1	....	Sol. Met.	....	....	....	....
Selenium.....	Se	79.2	Se₂	Sol. Non-met.	175	.685	.0762†	4.26
Silicon.......	Si	28.4	....	Sol. Non-met.	1400	....	.203†	2.34
Silver.......	Ag	107.93	....	Sol. Met.	955	....	.0570	10.5
Sodium......	Na	23.05	....	Sol. Met.	97.6	877.5	.293	.935
Strontium....	Sr	87.6	....	Sol. Met.	900	....	....	2.5
Sulphur......	S	32.06	S₈–S₂	Sol. Non-met.	117	444	.178‡	1.96
Tantalum....	Ta	183.0	....	Sol. Met.	2250	....	....	....
Tellurium....	Te	127.6	Te₂	Sol. Non-met.	452	1390	.0474	6.24
Terbium.....	Tb	160.0	....	Sol. Met.	....	....	....	....
Thallium....	Tl	204.1	....	Sol. Met.	301.7	1700	.0335	11.8
Thorium.....	Th	232.5	....	Sol. Met.	....	....	.0276	....
Thulium.....	Tm	171.0	....	?	....	....	....	...:
Tin.........	Sn	119.0	....	Sol. Met.	232	1525	.0562	7.3
Titanium....	Ti	48.1	....	Sol. Non-met.	3000	....	.1485	....
Tungsten.,..	W	184.0	....	Sol. Met.	1700	....	.0334	....
Uranium.....	U	238.5	....	Sol. Met.	800	....	.0277	....
Vanadium....	V	51.2	....	Sol. Met.	1680	....	....	....
Xenon.......	Xe	128.0	Xe	Gas. Non-met.	−140	−109	....	....
Ytterbium...	Yb	173.0	....	Sol. Met.	....	....	....	....
Yttrium.....	Yt	89.0	....	Sol. Met.	....	....	....	....
Zinc.........	Zn	65.4	Zn	Sol. Met.	419	918	.0955	7.1
Zirconium....	Zr	90.6	....	Sol. Non-met.	1500	....	.0662	....

* Yellow.   † Crystalline.   ‡ Rhombic.

TABLE VII

282. Table of heats of formation of some common compounds at normal temperature.

(The numbers refer to large calories.)

Substance	Heat of Formation			
	Gaseous	Liquid	Solid	Dissolved
Ammonia..................	+ 12.0	.....	.....	+ 20.4
Ammonia chloride........	.....	.....	+ 75.8	+ 71.9
Ammonium nitrate........	.....	.....	+ 88.0	+ 81.8
Barium carbonate........	.....	.....	+ 280.5	.....
Barium chloride..........	.....	.....	+ 194.7	+ 196.8
Barium oxide.............	.....	.....	+ 124.2	+ 158.7
Calcium carbonate........	.....	.....	+ 267.7	.....
Calcium hydroxide........	.....	.....	+ 214.2	+ 214.9
Calcium oxide............	.....	.....	+ 131.0	+ 149.5
Carbon dioxide...........	+ 97.6	.....	.....	+ 101.5
Carbon disulphide........	− 28.7	− 22.3	.....	.....
Cupric chloride...........	.....	.....	+ 51.6	+ 62.7
Cupric oxide..............	.....	.....	+ 37.2	.....
Hydrochloric acid..........	+ 22.0	.....	.....	+ 39.3
Hydrogen sulphide........	+ 2.7	.....	.....	+ 7.3
Lead oxide (PbO).........	.....	.....	+ 50.3	.....
Lead sulphide.............	.....	.....	+ 18.4	.....
Magnesium chloride.......	.....	.....	+ 151.0	+ 186.9
Magnesium oxide.........	.....	.....	+ 144.0	.....
Magnesium sulphate.......	.....	.....	+ 302.3	+ 329.0
Nitric acid...............	.....	+ 41.9	.....	+ 49.1
Nitrogen pentoxide........	.....	.....	+ 13.1	+ 29.8
Potassium carbonate......	.....	.....	+ 278.4	+ 284.9
Potassium chloride........	.....	.....	+ 105.6	+ 101.2
Potassium hydroxide......	.....	.....	+ 103.2	+ 116.5
Potassium nitrate.........	.....	.....	+ 119.5	+ 111.0
Potassium oxide..........	.....	.....	.....	+ 164.6
Potassium sulphate.......	.....	.....	+ 344.6	+ 338.2
Sodium bicarbonate.......	.....	.....	+ 227.0	+ 223.7
Sodium carbonate........	.....	.....	+ 269.9	+ 275.4
Sodium chloride..........	.....	.....	+ 97.6	+ 96.4
Sodium hydroxide........	.....	.....	+ 101.9	+ 111.8
Sodium nitrate...........	.....	.....	+ 111.3	+ 106.3
Sodium oxide.............	.....	.....	+ 100.2	+ 155.2
Sodium sulphate..........	.....	.....	+ 328.4	+ 329.0
Sulphur trioxide..........	.....	.....	+ 103.3	+ 142.5
Sulphuric acid.............	.....	+ 189.9	.....	+ 210.9
Water....................	+ 58.0	+ 68.0	+ 69.8	.....
Zinc sulphate.............	.....	.....	+ 230.0	+ 248.0

TABLE VIII

Tables of Length, Weight, and Volume

10 millimeters = 1 centimeter.
100 centimeters = 1 meter.
1 meter = 39.37 inches.
1 cubic centimeter of pure water at a temperature of 4° C. weighs 1 gram.
1000 grams = 1 kilogram.
1 kilogram = 2.2 pounds.
1000 cubic centimeters = 1 liter.
1 liter = 1.06 quarts.

Exact Equivalents

1 inch = 25.39954 millimeters.
1 liter = 35.197 fluid ounces.
1 ounce Avoirdupois = 28.34954 grams.
1 gram = 15.43235 grains.

APPENDIX

LABORATORY EQUIPMENT

In the following lists reference is made to certain firms by catalogue number. This is done for the purpose of being able to specify exactly the apparatus used. It should be understood that any supply house can furnish these things although they are specified according to the catalogue of another house.

Abbreviations: E. & A., Eimer and Amend; c.p., chemically pure; dil., dilute; conc., concentrated; com., commercial; cont., containing; s.g., specific gravity.

283. Student's individual equipment with approximate cost.

1 beaker, No. 2 Griffin's, with lip, Bohemian glass................$0.10
1 long right-angle bend, 8 cm. × 45 cm........................ .02
3 medium right-angle bends, 8 cm. × 15 cm.................... .06
3 short right-angle bends, 8 cm. × 8 cm........................ .04
2 500-c.c. bottles, 3.5 cm. across the mouth..................... .10
6 5-oz. flint-glass quinine bottles, 3.5 cm. across the mouth. Whit-
    all Tatum Co... .18
1 combustion spoon, ½ in.................................... .15

1 Royal Berlin porcelain evaporating-dish, 3 in.................$0.25
1 file, three-cornered, 4 in....................................... .10
1 carbon dioxide flask, holding 285 c.c. when filled to the brim,
    and measuring 3.5 cm. across the mouth.................. .15
1 pair of iron forceps, 4.5 in.   Eimer & Amend new catalogue, No.
    3335.. .09
1 funnel of glass, 2½ in....................................... .05
1 funnel-tube, 18 in.. .10
8 squares of glass, 2 in. square................................ .08
1 iron wire loop.   No. 18 standard wire gauge................... .01
1 mortar and pestle, E. & A., No. 4093, No. 7, 2½ in............. .25
1 glass stirring-rod.. .01
¼ lb. soft German glass tubing, inside diameter 5½ mm., outside
    diameter 7½ mm...................................... .10
3 2½-in. rubber connectors, made from ¼-in. rubber tubing, double
    thick, white stock................................... .06
1 8-in. piece of 3/16 in. black rubber tubing of pure gum, double thick .08
3 No. 8 two-hole rubber stoppers, small diameter, 33 mm......... .45
1 No. 3 one-hole rubber stopper.............................. .05
12 test-tubes, 6 in. × ¾ in..................................... .24
1 wire test-tube holder....................................... .10
1 wooden test-tube rack....................................... .25
3 pieces of copper wire...................................... .01

284. Equipment for general use.

One set of the following material should be constantly available at every laboratory position:

1000-c.c. wide-mouth bottle.................................$0.10
1 bulb test-tube.   Eimer & Amend, No. 4877................... .10
2 Bunsen burners with tubing................................. .70
1 foot rule with centimeter scale.............................. .10
1 square of cobalt glass, 4 in. × 4 in.......................... .10
1 500-c.c. filter-flask with tubing............................. .20
1 package of cut filter-paper, 10 cm. diameter.................. .10
1 brass filter-pump, E. & A., 3250............................ 1.25
1 50-c.c. graduated cylinder, double graduation................. .50
1 2-in. iron crucible, E. & A., 2879........................... .30
1 2-in. square iron plate with depression in centre............... .05
1 lamp-stand of iron.   Rod 18 in. high and ⅜ in. diameter....... .53
1 3-in. ring for stand.. .05
1 2-in. ring for stand.. .05
1 clamp for stand, E. & A., 2750.............................. .40
1 2-in. porcelain sieve funnel, E. & A., No. 3357................ .50
1 rubber stopper for funnel................................... .10
1 litmus paper bottle... .15

1 8-oz. conc. sulphuric acid bottle................................$0.23
1 8-oz. dil. sulphuric acid bottle.................................. .23
1 8-oz. conc. nitric acid bottle.................................... .23
1 8-oz. dil. nitric acid bottle...................................... .23
1 8-oz. conc. hydrochloric acid bottle............................ .23
1 8-oz. dil. hydrochloric acid bottle.............................. .23
1 8-oz. ammonium hydroxide bottle.............................. .23
1 8-oz. sodium hydroxide bottle.................................. .23
1 tin cup for shelf for water-pan, with hole in bottom and side..... .05
1 common centigrade thermometer, E. & A., 4894, graduated up
      to 130° C.. .50
1 bundle of toothpicks for splints............................... .05
1 water-pan, any kind of a rectangular pan over 4 in. deep........ .15
1 iron wire gauze with asbestos centre, E. & A., 7262............ .12
1 voltameter.. 7.00
1 Harvard trip scale, E. & A., 2142............................. 7.00
1 set of weights, E. & A., 2204, 1 g. to 500 g................... 2.25
1 test-tube cleaner with brush on end........................... .10

285. Additional apparatus of use in making up solutions and in making preparations.

Hot-plate..$5.00
2 8-liter flasks... 1.50
2 2½-liter flasks.. .80
1 12-in. Royal Berlin porcelain evaporating-dish................. 2.00
1 5-in. glass funnel... .30
1 Royal Berlin porcelain casserole, No. 6....................... 1.50
1 6-in. porcelain sieve funnel, E. & A., 3356.................... 2.00
6 No. 6 Griffin's beakers with lip............................... 1.20
1 sodium press...12.00

286. Reagents sufficient to enable a class of twenty students to perform the experiments in this book, with approximate cost.

Alcohol, 1 pint...$0.35
Aluminum foil, 1 oz... .10
Aluminum sulphate, 1 lb., c.p................................. .25
Aluminum wire, 1 oz... .10
Ammonium chloride, ½ lb...................................... .12
Ammonium nitrate, ½ lb....................................... .25
Ammonium sulphate, com., 2 lbs.............................. .20
Ammonium sulphide, made by passing hydrogen sulphide into am-
      monium hydroxide until saturated and then adding an equal
      volume of ammonium hydroxide.
Ammonium thiocyanate, 1 oz.................................. .05
Arsenic, metal, ½ lb.. .30

Arsenic trioxide, ¼ lb...$0.10
Barium chloride, c.p., 2 oz....................................... .05
Barium nitrate, com., ¼ lb .... .10
Borax, 1 lb.. .10
Bromine water, made by shaking liquid bromine with water and
    keeping an excess of bromine in bottle.
Bromine, 2 oz... .25
Cadmium sulphate, 1 oz .... .20
Calcium chloride, com., ½ lb..................................... .05
Calcium nitrate, com., 1 oz...................................... .15
Calcium oxide, lime, 2 lbs....................................... .05
Carbon disulphide, 2 lbs... .44
Charcoal, animal, 1 lb... .02
Charcoal, wood, 1 lb... .01
Chloride of lime, 1 lb... .05
Chlorine water..
Chrome alum, ¼ lb... .05
Coal, bituminous, 3 oz..
Copper, sheet, 1 lb... .40
Copper wire, No. 18 standard wire gauge, ¼ lb.................. .10
Copper gauze, 80 mesh, 10 g..................................... .20
Copper scale, ¼ lb.. .10
Copper sulphate, com., 1 lb..................................... .10
Cream of tartar, 1 lb... .35
Ferrous sulphate, com., 2 lbs................................... .06
Ferrous sulphide, com., lumps, 5 lbs............................ .50
Grape-sugar, 1 oz... .02
Hydrofluoric acid, 4 oz... .50
Iodine, 1 oz.. .25
Iron filings, ½ lb.. .05
Iron wire, fine, 2 lbs.. .10
Iron wire, 2 lbs. No. 16 standard wire gauge.................... .20
Lead nitrate, com., 1 oz.. .02
Lead oxide, litharge, ¼ lb...................................... .03
Lead oxide, red lead, 1 oz...................................... .03
Lead wire, 1 oz... .05
Magnesium oxide, ½ lb... .25
Magnesium wire, 1 oz.. .55
Manganese dioxide, 1 lb., powder................................ .08
Marble, 1 lb.. .10
Mercury, 1 oz... .10
Mercuric chloride, 2 oz... .20
Mercuric oxide, red, 2 oz....................................... .20
Oxygen mixture, made by mixing two parts of pulverized potassium
    chloride with one part of powdered manganese dioxide, 1 lb. .30
Phosphorus, red, 1 oz... .10

Phosphorus, yellow, 1 oz..$0.10
>   This phosphorus should be granulated as follows:
>   Stand a 9-liter flask having a cylindrical neck at least 2 in.
> in diameter in the sink, and fill it with cold water up to the
> beginning of the neck.
>   Contract the end of a 1-in. carbon filter-tube, by heating,
> to a ⅛-in. hole.   Push this end barely through the centre of
> a disk of sheet cork just a little larger than the diameter of the
> neck of the flask.   Now push the cork in a horizontal position
> down into the neck of the flask until the filter-tube is entirely
> within the neck, the top of the tube being about 1 in. below
> the top of the flask.   Add cold water through the tube until
> the surface reaches the cork, and fill the neck with boiling
> water.   Cut up all the stick phosphorus into pieces not more
> than 1 in. long, and quickly drop them one at a time into the
> filter-tube.   They will melt almost at once and run down into
> the flask in the form of shot.   The first to go through will
> probably go into the undercooled condition and operations
> must be suspended until they crystallize.   Add boiling water
> to the neck of the flask from time to time.   A pound of phos-
> phorus can be made into thousands of pellets in this way in less
> than half an hour.   Reasonable caution must be used in han-
> dling so much phosphorus.

Potassium alum, ½ lb...................................... .10
Potassium bromide, c.p., 2 oz................................. .20
>   chloride, c.p., ½ lb................................. .15
>   chlorate, c.p., ½ lb................................ .10
>   chromate, 1 oz..................................... .05
>   dichromate, ½ lb................................... .07
>   ferrocyanide, c.p., 1 oz............................. .02
>   ferricyanide, c.p., 1 oz............................. .05
>   hydroxide, pure by alcohol in sticks, 1 oz.............. .10
>   iodide, c.p., 1 oz.................................. .30
>   nitrate, com., 1 lb................................. .05
>   permanganate, 1 oz................................ .05
>   sulphate, 1 oz..................................... .05
>   tartrate, normal salt, ½ lb.......................... .40

Quinine sulphate, ¼ oz...................................... .10
Sand, 1 oz.. .01
Silver nitrate, 1 oz... .50
Silver wire or foil, 6 g...................................... .20
Sodium bicarbonate, c.p., 1 lb............................... .20
>   carbonate, soda-ash, 2 lbs.......................... .10
>   chloride, table salt, 2 lbs........................... .05
>   nitrate, com., 1 lb................................. .10
>   nitrite, com., 1 lb.............   .... .10

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        phosphate, common cryst., 1 lb...........................$0.10
        sulphate, com. Glauber salt, 1 lb........................  .03
        thiosulphate, 1 lb.......................................  .05
Sodium, metal, 1 oz..........................................  .25
Sodium wire—this is made when needed by means of a sodium press.
Stannous chloride, made when needed by dissolving tin in hydro-
        chloric acid.
Starch, corn-starch, 1 lb....................................  .10
Strontium nitrate, com., ½ lb................................  .07
Sulphur, brimstone, 3 lbs....................................  .15
Tartaric acid, ½ lb..........................................  .15
Tin, granulated, ¼ lb........................................  .15
Water-glass, ½ lb............................................  .05
Zinc, granulated, 2 lbs......................................  .40
        oxide, ¼ lb..........................................  .03
        sulphate, ¼ lb.......................................  .02
```

287. Stock acids and solutions for a class of twenty, for which it is desirable to have special reagent bottles.

Sulphuric acid, conc., c.p., specific gravity 1.84, cont. 98% acid,
        10 lbs...$0.80
Sulphuric acid, dil., made by mixing one part of the conc. acid with
        three parts of distilled water, s.g. 1.28, cont. 38.13% acid.
Nitric acid, conc., c.p., s.g. 1.42, 8 lbs........................... .80
Nitric acid, dil., made by mixing the conc. acid with an equal
        volume of water, s.g. 1.28, cont. 45.55% acid.
Hydrochloric acid, conc., c.p., s.g. 1.2, cont. 40% acid, 8 lbs..... .80
Hydrochloric acid, dil., made by mixing equal volumes of the conc.
        acid and distilled water, s.g. 1.1, cont. 19.8% acid.
Ammonium hydroxide, conc., c.p., s.g. .90, 2 lbs................. .20
Ammonium hydroxide, dil., made by mixing one volume of conc.
        ammonia with three vols. of water, s.g. .97, and cont. 15%
        ammonium hydroxide.
Sodium hydroxide solution, conc., made by dissolving 1000 g. com-
        mercial granulated sodium hydroxide in 1000 c.c. of water
        in an iron dish, allowing the solution to settle for a week and
        siphoning off the clear solution; s.g. 1.51, and cont. 51%
        sodium hydroxide.   2 lbs. crude NaOH................... .20
Sodium hydroxide solution, dil., made by diluting one volume of
        the conc. solution with three vols. of water; s.g. 1.18 and
        cont. 16% NaOH.
Alcohol, ethyl, 95%.
Ammonium sulphide.
Barium chloride, 10% solution.
Bromine water, saturated with bromine.

Calcium hydroxide, saturated solution made when wanted.
Carbon disulphide.
Chlorine water.   Made when wanted.
Copper sulphate, 10% solution.
Lead nitrate, 10% solution.
Litmus solution, made by dissolving about 1 g. of azolitmin in 2 liters of distilled water and filtering.
Mercuric chloride, 5% solution.
Potassium chromate, 10% solution.
Potassium dichromate, 10% solution.
Potassium ferrocyanide, 10% solution.
Potassium iodide, 5% solution.
Potassium permanganate, 10% solution.
Silver nitrate, 5% solution.
Sodium phosphate, 10% solution.
Stannous chloride, 10 g. of tin to 100 c.c. of acid.

PART IV

DESCRIPTIVE

CHAPTER XXI

TOPICS WHICH SHOULD BE DISCUSSED IN THE DESCRIPTION
OF ANY SUBSTANCE

288. Brief outline of topics.

1. Appearance and state.
2. Occurrence.
3. Physical properties.
4. Chemical properties, including method of recognition.
5. Preparation.
6. Uses.
7. Common compounds.

289. Appearance and state. What it looks like, its color, and whether it is a solid, liquid, or a gas under normal conditions.

290. Occurrence. If it is an element, it may or may not be found in the free condition. If it does occur in the free condition, state where and in what quantity. If it occurs only in the combined condition, state where, as what, and in what quantity.

291. Physical properties.

(*a*) **Solid.** How it behaves when heated out of contact with the air; that is, will it melt, boil, vaporize, or sublime, and under what conditions? Will it dissolve in water or in other liquids and to what extent? It is convenient to recognize three degrees of solubility; very soluble, soluble, and virtually insoluble. What is its specific gravity; that is, how heavy is it compared with water?

(*b*) **Liquid.** Effect of cooling or heating out of contact with air. At what temperature does it freeze or boil? Does

it dissolve in water or other liquids? Does it act as a solvent for other substances? How heavy is it compared to water?

(c) **Gas.** How does its volume change with a change of temperature? (**155**). How does its volume change with the pressure? (**156**). How soluble is it in water or other liquids? What is the weight of a liter of the gas at normal temperature and pressure? The weight of a liter of a gas is approximately equal to half of its molecular weight in grams multiplied by .09. Or it is equal to its molecular weight in grams divided by 22.4 (**216**). What volume does a gram-molecular weight occupy? (**216**).

292. Chemical properties.

(a) **Element.** Does it burn or support combustion? What oxides does it form? (**95–103**). Are these oxides basic or acidic? (**95–103**). What bases or acids do these oxides form with water? (**95–103**). What compounds does it form with hydrogen or other elements? What experiments might be done with it? What is the common test for it in the free condition? in the combined condition? (**305**).

(b) **Compound.** Does it burn or support combustion? How may it be decomposed? What chemical changes does it take part in? What experiments might be performed with it? What are the common tests for the elements or radicals it contains?

293. Preparation.

(a) What is a common method for its preparation in the laboratory?

(b) What is the common method of its commercial preparation?

(c) State two other methods for its preparation.

294. Uses.

(a) How is it used in the industries?

(b) Is it used in medicine?

(c) **Is it used in the household? for what?**

295. Common compounds, if it is an element. Mention the common compounds of the element which have not already been touched upon, giving the **chemical name** and **formula,** the **common name,** and the **mineral name.**

CHAPTER XXII

OXYGEN

296. Appearance and state. Oxygen, in the normal form, is a colorless gas; in the liquid and solid forms it is light blue.

297. Occurrence. It occurs in the free condition in the atmosphere, forming about one-fifth of the air by volume. In the combined form it makes up about one-half the weight of the earth. Water is eight-ninths oxygen by weight, and sand a little more than one-half.

298. Physical properties. It is normally a colorless, odorless, and tasteless gas, slightly heavier than air. At **normal temperature and pressure** (760 mm. pressure and 0° C. temperature) 1 liter weighs 1.43 g. It is slightly soluble in water; 4 volumes of the gas dissolve in 100 volumes of water at 0°. At constant temperature its volume varies inversely as the pressure (Boyle's law) (**155**); that is, under ordinary conditions, if the pressure be doubled, the temperature being kept constant, the volume will be reduced to one-half. At 0° C. and at constant ordinary pressure the volume will increase 1/273 of the original volume at 0° for every increase of 1° in temperature. Thus, if we had 273 c.c. of oxygen at a temperature of 0° C. and a pressure of 760 mm., and the temperature were increased to 274° C., the volume would become 274 c.c. Also, if the temperature were decreased 273° C., the volume would theoretically disappear. This point, 273° below zero, is known as **absolute zero,** and temperatures reckoned therefrom **absolute temperatures.** If the given temperatures be changed to absolute temperatures by adding 273, then it may be said that (by Charles's law) **the volume of a body of gas at constant pressure varies directly as its absolute temperature** (**157**).

299. Chemical properties. Oxygen combines directly or indirectly with most of the elements, forming compounds called **oxides.** In many cases, when once started, this combination

253

goes on spontaneously and is accompanied by light and heat. Substances that burn in air burn very much more readily in oxygen. Such substances are called **combustible bodies,** and oxygen is said to be a **supporter of combustion.** It is evident that for ordinary combustion two substances are necessary, one of which must be oxygen and the other a combustible body. If this combustible body happens to be a gas with which oxygen combines readily, it ought to be possible to reverse the conditions and have oxygen appear to burn in an atmosphere of that gas. Hydrogen burns readily in oxygen. If a jar of hydrogen be inverted, the gas ignited at the mouth, and a slow stream of oxygen issuing from the end of a tube be thrust up through the hydrogen flame, the oxygen appears to burn in the jar (Fig. 47).
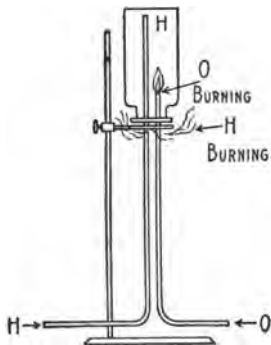
Fig. 47

When oxygen combines with hydrogen, hydrogen oxide, or water, is formed. This appears as moisture on the inside of the jar.

If a splint of wood having a spark on the end be introduced into a jar of oxygen, the spark instantly bursts into flame. Sulphur which burns with a faint blue flame in air burns very much more brightly in oxygen. The product in this case is chiefly a colorless gas with a very disagreeable odor and is an oxide of sulphur. Even iron, in the form of braided picture-wire, will burn energetically with bright scintillations, provided some kindling material be attached to the end and first ignited. The product in this case is a steel-blue solid which drops from the end of the wire in small globules. This product is called **magnetic oxide of iron** (Fig. 48).
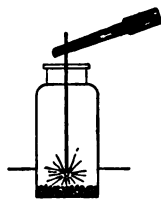
Fig. 48

300. Preparation. In preparing any element we usually have to make use of some compound of it. This compound must be as cheap as possible and at the same time admit of the preparation of the element from it

Fig. 49. Battery of 100 Burdett Cell Electrolytic Oxygen Generators

in a simple manner and at slight cost. It would seem that, as oxygen occurs free in the air in large quantity, we might readily obtain it from that source. It is, however, intimately mixed with large quantities of nitrogen, and the process of separating it is neither simple nor cheap. Oxygen constitutes eight-ninths the weight of water and may be easily obtained from it by passing an electric current through a water solution of certain substances. This method has recently come into extensive use (Fig. 49).

301. **Laboratory method of preparation.** It is found that certain substances when heated give up part or all of their oxygen. A compound of mercury and oxygen known as mercuric oxide gives up all of its oxygen when heated, and pure mercury is left. A compound of manganese and oxygen, known as manganese dioxide, gives up part of its oxygen, and a compound of potassium, chlorine, and oxygen, known as potassium chlorate, gives up all of its oxygen, if it is heated enough. As this latter material gives more oxygen at a less cost than other available materials, it is the one most commonly used in the laboratory. When this substance is heated alone it melts at about 350° and soon apparently begins to boil. This boiling is due to the escape of the oxygen from the liquid. It is found that if powdered manganese dioxide be mixed with the powdered potassium chlorate, the reaction goes on at a very much lower temperature and at the end of the action the manganese dioxide is left unchanged, mixed with a compound of potassium and chlorine known as potassium chloride. The black oxygen mixture commonly used contains from one-fourth

Fig. 50

to one-half manganese dioxide, intimately mixed with powdered potassium chlorate. The apparatus may be arranged as shown
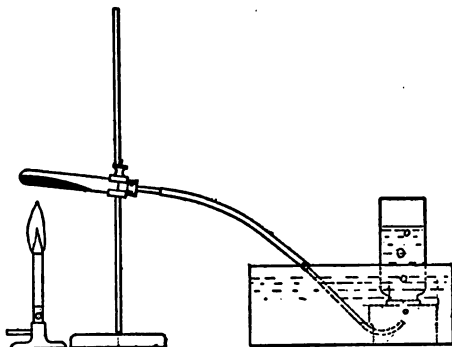
in Fig. 50. It is unnecessary to melt the glass test-tube. The gas is collected over water in a water-pan, as indicated.

302. Method of manufacture. When barium oxide is heated in the air to 500° it absorbs more oxygen, forming a new compound; if this compound be heated still hotter, it gives up the extra oxygen, leaving the original barium oxide. This is the basis of a continuous process for extracting oxygen from the air.
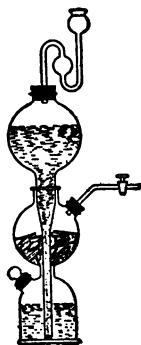
Other methods. A continuous supply of oxygen may be obtained by allowing water to react with sodium peroxide in a suitable apparatus, such as a Kipp generator (Fig. 51); also, water containing some dissolved caustic soda might be electrolyzed (Fig. 49).

303. Common compounds. Oxygen unites with nearly all the elements, forming compounds known as oxides. These oxides, in many cases, unite with each other or with other substances, forming compounds containing more than two elements. Some of the more common compounds are the following: **water, sand, carbon dioxide, sulphur dioxide, iron oxide, sulphuric acid,** and **caustic soda.**

Fɪɢ. 51

304. Uses. The gas is used with hydrogen in a special form of burner for the purpose of producing the **oxyhydrogen flame.** This flame has a very high temperature and can be used for melting platinum or producing the lime light. The gas is also administered to patients in the last stages of certain diseases, frequently with beneficial results.

305. Chemical tests. A chemical test is a process by means of which a minute quantity of a substance may be recognized as being present. It usually makes use of some characteristic property of the substance in question, especially in forming some new substance, very small quantities of which may be recognized. It is often necessary to apply several different tests in order to be sure of the presence of the material in question.

306. Test for oxygen. Oxygen, if present in the nearly pure condition, is usually recognized by introducing a spark on the end of a splint. If the gas is present the splint will either con-

tinue to burn as a spark or will burst into flame. If colorless nitric oxide gas be introduced into a bottle containing oxygen, the mixture will turn brown.

307. **Ozone** is a modification of oxygen, containing three atoms in the molecule. It is a powerful oxidizing agent on account of the ease with which it breaks up into inert molecular oxygen and active atomic oxygen, according to the equation:

$$O_3 = O_2 + O.$$
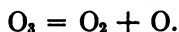
This gas has a peculiar odor which is always noticeable about electric machines where there is any arcing or disruptive discharge.

It is made by passing a current of air or oxygen through a glass tube across which a silent discharge from an induction-coil is taking place (Fig. 52).
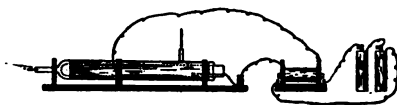
FIG. 52

Water may be purified by causing ozonized air to bubble through it. In many public buildings ozonized air is introduced into the ventilating systems with very beneficial results.

308. **Relation of oxygen to life.** The body heat of all animals is maintained by the gradual oxidation of the tissues of the body by means of oxygen which has entered the blood through the lungs. With each breath some of the oxygen drawn in passes through the walls of the lungs and combines with the blood, rendering it bright red. This red, or arterial, blood is pumped by the heart through the arteries into the capillaries, passages existing in all parts of the body so small that but one corpuscle can pass at a time. During the passage through these capillaries the oxygen of the blood oxidizes such portions of the tissue as are ready for oxidation, forming products that are easily eliminated from the body, especially carbon dioxide and water.

The carbon dioxide combines with the blood, rendering it dull red, and the blood passes on into the veins and back to the heart. The heart pumps it into the lungs, where it gives up its carbon dioxide and absorbs more oxygen. The exhaled breath contains nitrogen, water vapor, carbon dioxide, and some oxygen.

CHAPTER XXIII

COMBUSTION, BURNING, AND FLAME

(Laboratory Exercises No. 3, 4, 5)

309. Combustion has already been defined as a rapid chemical combination accompanied by light and heat. Two substances are necessary, and it is only essential that enough heat be set free, after the action is once started, to maintain it to the end.

A mixture of finely divided sulphur and iron, when heated sufficiently to start the action, will become red-hot and will remain so until either all of the sulphur or all of the iron has entered into chemical combination. The product formed is called iron sulphide.

A jet of chlorine gas will not burn in air, but will burn readily if it is once ignited in an atmosphere of hydrogen, the product formed being hydrogen chloride.

Antimony in the powder form, when sprinkled into a jar of moist chlorine, instantly bursts into flame, forming antimony trichloride.

310. Burning is a form of combustion in which oxygen is one of the combining substances. The materials which burn readily in the air are called **combustible bodies**. It is usually necessary to heat the combustible substance in contact with oxygen or air, in order to start the action; and if sufficient heat is set free, the burning will continue until the fuel is used up.

Hydrogen, lithium, sodium, potassium, magnesium, calcium, aluminum, carbon, phosphorus, sulphur, and iron, when once ignited, burn with great readiness in air and with great violence in moist oxygen, forming oxides.

If the combustible substance is a gas, it always burns with a flame which is either luminous or non-luminous. But even so-called non-luminous flames give sufficient light to be quite visible in the dark.

If the burning substance is a compound or mixture, the products formed are usually the oxides of the combustible elements contained in it.

Illuminating gas is a mixture containing several combustible compounds of carbon and hydrogen, among them being methane and ethane. When these burn, water and carbon dioxide are formed.

Kerosene is a mixture of a great many similar compounds, all of which contain carbon and hydrogen, and when it burns the products are chiefly carbon dioxide and water.

If a large dry bottle be held over a small gas flame for a few moments, it will become covered with moisture on the inside; and if some lime-water be placed in the bottle and the bottle shaken, the lime-water will turn white, showing the presence of carbon dioxide.

311. Kindling temperature. The temperature to which a substance must be raised before it will take fire and continue to burn by itself is known as its kindling temperature. Phosphorus has a very low and iron a very high kindling temperature.

312. Flame. A flame is a burning gas. A combustible liquid must first be heated hot enough to convert some of it to a gas, and then this gas must be heated to its kindling temperature before it will take fire. If a solid burns with a flame, it is either because it is converted to a gas by the heat or because it gives off a combustible gas. When a candle is lighted the grease on the wick is first converted to a gas. The burning gas melts more grease, which in turn takes fire. If the end of a glass tube be inserted in a candle flame, the unburnt candle gas will issue from the other end and may be ignited (Fig. 53). If some bits of wood or paper be placed in a glass tube and heated, a combustible gas will issue from the end of the tube and may be ignited (Fig. 54).

FIG. 53

FIG. 54

313. The Bunsen flame. In the Bunsen burner the jet of gas issuing from the inner tip draws air in through the two holes
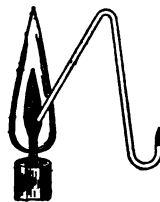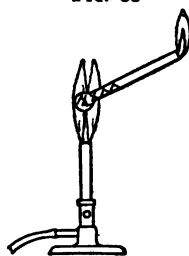
at the base and forms a combustible mixture of gas and air. This burns at the top with a blue flame. A close examination of this flame shows that it consists of two parts, or cones (Fig. 55). The inner cone consists of unburnt gas, while the outer is the region of the actual burning. The hottest part is just above the top of the inner cone. If the gas supply be partly shut off, there will be too large a supply of air and an explosive mixture results. In this case the flame "snaps back" and burns at the base.

Outer Cone
Hottest Part
Inner Cone
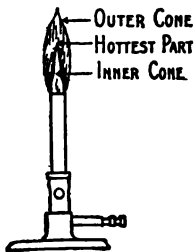
Fig. 55

314. The Davy safety-lamp. If a wire gauze be suddenly moved from the top down half-way through a Bunsen flame, the flame will not pass through it at once, for the reason that the burning gases are cooled by the gauze below the kindling temperature. If the gauze be held over a burner, the gas turned on and ignited above the gauze, the flame will not pass through to the lower side (Fig. 56). This principle is made use of in the Davy safety-lamp, which is used in mines where there are combustible gases. The gases pass through the wire gauze and burn inside
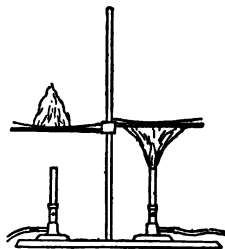
Fig. 56
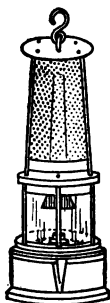
the lamp, but the flame cannot travel through and ignite the gases in the mine (Fig. 57).

315. Oxidation is the combining of oxygen with any substance. All cases of ordinary burning are cases of oxidation. There are many cases of oxidation, however, in which there is no sensible heat or light.

Iron rusts in moist air, and just as much heat is formed as though it had been burned rapidly to the same product; but the action takes place through such a long time that the heat is not noticeable.

Fig. 57

Animal and vegetable substances decay largely on account of being oxidized, and often produce sensible heat.

Many vegetable oils combine with oxygen forming a hard product, and the oil is said to dry.

316. Spontaneous combustion. The temperature reached in any case of oxidation is simply a question of how fast the heat formed can escape.

If the heat can escape as fast as it is formed the temperature will not rise appreciably. If, however, the oxidizable substance is so situated that the heat will accumulate, the rate of oxidation will increase, the temperature of the material will soon reach its kindling point, and the substance will burst into flame. This is the cause of a great many fires and is called **spontaneous combustion. Oily rags and cotton waste, if left in a place where there is little circulation of air, are very apt to take fire.** The oily dust of flour mills sometimes ignites with explosive violence. Bituminous coal should never be stored in very large piles or in unventilated bins, for it is sure to take fire by spontaneous combustion.

Questions

1. What is combustion? Give examples of it (309).
2. What is burning? If a compound of carbon and hydrogen burns, what products are formed? (310). What is a combustible body? a supporter of combustion? (310).
3. What is flame? Describe the Bunsen flame (312–313).
4. What is oxidation? What becomes of the heat of oxidation? (315).
5. What is spontaneous combustion? What classes of bodies are subject to spontaneous combustion? (316).

CHAPTER XXIV

Hydrogen

(Laboratory Exercise No. 6)

317. Appearance and occurrence free. Hydrogen is a colorless, odorless, and tasteless gas. It does not occur to any appreciable extent in the free condition on the earth, although there is a minute quantity in the air. The atmosphere of the sun, however, contains a very large quantity.

318. Occurrence combined. It forms one-ninth of water by weight and is contained in all animal and vegetable tissues and in all petroleum and coal-tar products.

319. Physical properties. It is the lightest of all known substances, being sixteen times lighter than oxygen. One liter of hydrogen weighs .0896 g. at 0° and 760 mm. The volume of a body of hydrogen increases 1/273 of the corresponding volume at 0° for every increase of 1° in temperature. At constant temperature its volume varies inversely as the pressure.

With sufficient pressure and cold it condenses to a colorless liquid. And at still lower temperature it changes to a white solid.

Its critical temperature is — 243° and the critical pressure is 15 atmospheres (164). It is almost insoluble in water, 100 c.c. of water dissolving about 2 c.c. of the gas.

320. Chemical properties. Hydrogen burns with an almost colorless flame in oxygen or air, forming water:

$$2 H_2 + O_2 = 2 H_2O.$$
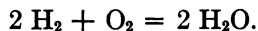
It will support the combustion of those gases with which it combines readily. A jet of chlorine introduced into an inverted receiver filled with hydrogen which is burning at the mouth takes fire and burns in the receiver, forming hydrogen chloride:

$$H_2 + Cl_2 = 2 HCl.$$
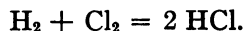
In a similar way hydrogen will support the combustion of
oxygen. Several metals absorb a large volume of the gas.
Finely divided platinum will take up 50 volumes of the gas,
and palladium has been known to absorb over 800 volumes.
If a jet of hydrogen be directed against a piece of sponge
platinum, it immediately bursts into flame. The platinum,
acting as a **catalytic agent,** brings about the rapid oxidation of
the hydrogen.

A mixture of 2 volumes of hydrogen to 1 volume of oxygen
is known as **detonating gas.** When this mixture is ignited it
explodes with great violence.

Hydrogen is a powerful reducing agent, and at a high tempera-
ture will extract the oxygen from many oxygen compounds,
especially the oxides of the metals, forming water and setting
the metal free:

$$PbO + H_2 = Pb + H_2O.$$
$$Fe_2O_3 + 3 H_2 = 2 Fe + 3 H_2O.$$
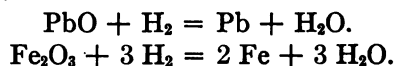
321. Test. The gas is burned and the products passed
through a condenser. The appearance of water indicates that
the gas contained hydrogen.

322. Preparation. (1) Hydrogen is commonly made in the
laboratory by the action of zinc on dilute sulphuric acid. The
zinc displaces an equivalent quantity of hydrogen in the acid,
setting it free and forming zinc sulphate:

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$
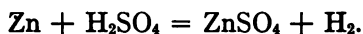
A bottle fitted with a two-hole stopper through which passes a
funnel-tube and delivery-tube makes a perfectly satisfactory
generator. Granulated zinc, made by pouring very hot molten
zinc into water, is placed in the bottle and dilute sulphuric
acid (1 volume of acid to 5 volumes of water) is added through
the funnel-tube.

It is well also to pass the gas through a wash-bottle contain-
ing water to remove the spray (Fig. 58). A jet of hydrogen
coming from a generator should never be ignited until it is
certain that all of the air has been removed. Otherwise there
may be a dangerous explosion.

(2) Hydrogen may also be prepared by the action of other

metals with other acids.   It is only necessary that the solution pressure (197) of the metal be greater than that of hydrogen.   Thus, iron with hydrochloric acid gives the gas:

$$Fe + 2 HCl = FeCl_2 + H_2.$$
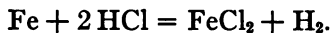
If a metal be dissolved in nitric acid, the hydrogen is usually oxidized to water and does not appear in the free condition.

(3) Sodium and potassium decompose water at the ordinary temperature, setting hydrogen free and forming the corresponding hydroxides:

$$2 Na + 2 HOH = 2 NaOH + H_2.$$
$$2 K + 2 HOH = 2 KOH + H_2.$$

FIG. 58
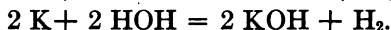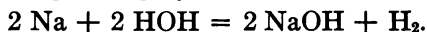
(4) When steam is passed over red-hot iron, hydrogen is set free.   The oxygen combines with the iron, forming magnetic oxide:

$$4 H_2O + 3 Fe \leftrightarrows Fe_3O_4 + 4 H_2.$$
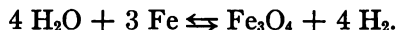
This is a reversible reaction.   If an excess of hydrogen were passed over the oxide, water and metallic iron would be formed.

(5) Hydrogen may also be prepared by the electrolysis of water containing a little sulphuric acid (Fig. 59).

323. Uses.   When hydrogen burns in oxygen or air it produces a very hot flame.   If this flame be directed against an infusible substance, such as a piece of quicklime, a very intense white light, called the **lime-light,** is produced.

On account of its lightness hydrogen is used in large balloons.   The lifting power of the gas would be equal to the difference between the weight of a given volume and the weight of an equal volume of air.   One liter of the gas would have a lifting power of about 1.2 g.
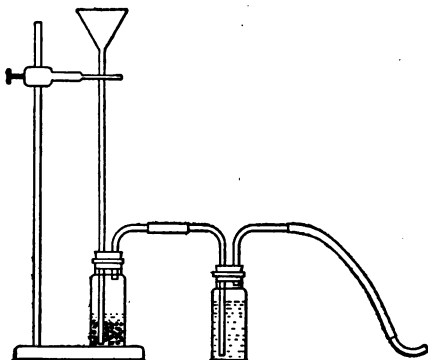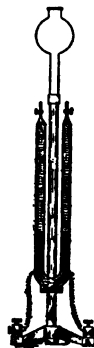
FIG. 59

324. Common compounds. Hydrogen oxide, or water, H_2O; marsh-gas, CH_4; and all petroleum products—**benzole, C_6H_6,** and all coal-tar products; **hydrochloric acid, HCl; sulphuric acid, H_2SO_4; nitric acid, HNO_3;** and all other acids.

CHAPTER XXV

WATER AND HYDROGEN PEROXIDE

Water (Laboratory Exercise No. 9)

325. Appearance, state. Pure water is a colorless liquid when seen in thin layers, but in very large masses it appears blue. If a long, straight pipe provided with plate-glass ends be filled with pure water, the blue color may be readily seen.

326. Occurrence free. Water is one of the commonest natural compounds on the earth. Without it all chemical reactions would cease, and life itself would become extinct. It occurs naturally in seas, rivers, lakes, springs, and as rain, snow, and hail. These different kinds of natural waters have different properties or qualities in accordance with the kind of material with which they have been in contact. Rain or snow is the purest form of natural water, especially that which has fallen during the last part of a storm. In any case, it will be contaminated only with the dust or gases of the air.

(1) **Spring-water.** The rain-water soaks into the earth, gradually dissolving the substances with which it comes in contact, and finally appears as spring or well water. This is usually perfectly clear, as it should be, for the water has been well filtered; but it must contain dissolved substances of many kinds, for it has been gradually percolating through the sand and rocks of the surrounding country.

(2) **River-water.** Rivers usually have their origin in springs and are also fed by surface drainage. They not only contain the original dissolved impurities of the springs, but also quantities of suspended impurities, finely divided matter that does not at once settle out as a sediment. Such water usually has to be filtered to remove the sediment before it is fit to drink.

(3) **Fresh-water lakes.** Lake water is very pure and free from suspended impurities, for the reason that the velocity of the river, which has been sufficient to keep the sediment in suspension, is lost and the particles of suspended matter have a chance to settle, leaving nothing in the water but the dissolved impurities obtained from the springs and surface drainage. All fresh-water lakes have outlets.

(4) **Salt lakes.** If a lake has no natural outlet, it is usually because the natural evaporation is equal to or greater than the rate at which water is flowing into the lake. In the course of years this would result in the lake becoming a strong solution of various kinds of salts. The

ultimate complete evaporation of such lakes in past geological ages accounts for many of the existing large deposits of salt.

(5) **Sea-water.** The various oceans are the ultimate reservoirs into which most of the rivers of the land flow. The waters of the ocean have not only been washing the land for countless years, but, by the continual process of evaporation from its surface and the condensation and precipitation of this moisture in the form of rain and snow, solid materials from the land are constantly being dissolved and washed into the sea.

By far the most abundant substance contained in the sea-water is common salt. Many other salts are present, however, in appreciable quantities, and it is undoubtedly true that there is not a known element that could not be found in the sea-water.

327. Occurrence combined. Many substances when crystallizing from water solution combine chemically with a definite quantity of water. This water seems to be necessary for the crystalline form and color. Such substances when heated give up part or all of the water. Water combined in this way is known as **water of crystallization.**

Water also occurs as an essential ingredient of all animal and plant tissue. It is also present in all substances that have ever been exposed to the air.

328. Physical properties. At a pressure of 760 mm., that is, at the pressure due to the weight of the atmosphere at the sea-level, water boils at a temperature of 100°. It freezes at a temperature of 0°. It possesses its maximum density at a temperature of 4°, and the amount of matter in 1 c.c. of water at this temperature is taken as the unit of mass, which is called a **gram.** The amount of heat necessary to raise the temperature of 1 g. of water 1° is called a **calorie.**

If 1 g. of ice at a temperature of 5° below freezing be slowly heated it will gradually expand while still in the solid form until the temperature reaches 0°, it will then begin to melt and the temperature will remain at 0° until it has all melted. During this time 79 calories of heat will be required to melt it. The volume of the resulting water at 0° will be about .09 c.c. less than the ice was at that temperature. As the heat is still added the volume again contracts until the water reaches its maximum density at 4°. Beyond this point it expands slowly until the temperature of 100° is reached. The amount of heat necessary to raise the temperature of the 1 g. of water at 0° to 100° is 100 calories. At 100° the temperature remains constant, until all the water has been changed into steam. The amount of heat necessary to change 1 g. of water at 100° to steam at 100° is known as the **latent heat of steam,** and is equal to 537 calories.

Pure water is a non-conductor of the electric current.

329. Chemical properties. Water is the most important chemical compound known to mankind. It is directly or indirectly concerned in most chemical reactions. In many of these it simply plays a mechanical part; that is, it simply brings about or aids a given chemical change. A substance that either brings about or aids a chemical change without undergoing any chemical change itself is called a **catalytic agent.**

Most of the reactions of the chemical laboratory take place in water solution, the water playing the part of a catalytic agent and undergoing no change itself. It unites with many substances when they are being separated from solution, as water of crystallization, forming what are known as **hydrates.** Thus, we have crystallized copper sulphate, or blue vitriol, which contains 5 molecules of water of crystallization; also crystallized sodium sulphate, or **Glauber's salt,** containing 10 molecules of water of crystallization.

Water unites directly or indirectly with most of the oxides of the elements, forming two large classes of compounds known as acids and bases. The oxides of the non-metals form the acids, and the oxides of the metals form the bases. Thus we have:

$$SO_3 + H_2O = H_2SO_4, \text{ sulphuric acid.}$$
$$N_2O_5 + 2\,H_2O = 2\,HNO_3, \text{ nitric acid.}$$
$$P_2O_5 + 3\,H_2O = 2\,H_3PO_4, \text{ orthophosphoric acid.}$$
$$Na_2O + H_2O = 2\,NaOH, \text{ sodium hydroxide, a base.}$$
$$CaO + H_2O = Ca(OH)_2, \text{ calcium hydroxide, a base.}$$
$$BaO + H_2O = Ba(OH)_2, \text{ barium hydroxide, a base.}$$
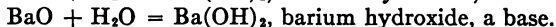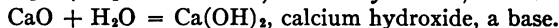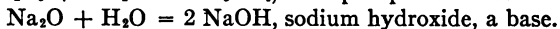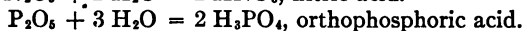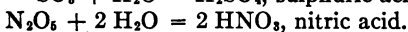
330. Decomposition of water. Many substances decompose water either at the ordinary temperature as water, or at high temperatures when it is in the form of steam. Sodium and potassium react with water at the ordinary

FIG. 60

temperature with the evolution of hydrogen and the formation of the corresponding base:

$$2\,Na + 2\,H_2O = 2\,NaOH + H_2.$$
$$2\,K + 2\,H_2O = 2\,KOH + H_2.$$
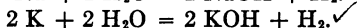
If a long tube be filled with iron wire or nails and heated to a high temperature in a suitable furnace, steam when passed through the tube will give up its oxygen to the iron, and hydrogen will issue from the other end (Fig. 60):

$$4\,H_2O + 3\,Fe = Fe_3O_4 + 4\,H_2.$$
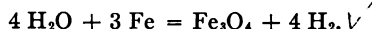
Again, in a similar way, if the tube be filled with carbon, and steam be passed through the hot tube, the oxygen of the steam will combine with

the carbon, forming carbon monoxide, and the mixed gases will issue from the other end of the tube. This mixture of carbon monoxide and hydrogen is known as **water-gas:**

$$C + H_2O = H_2 + CO.$$
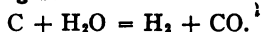
At very high temperatures water is partly decomposed into oxygen and hydrogen.

Although pure water cannot be decomposed by the electric current, yet, when it contains in solution certain substances, especially the common acids, bases, and salts, it is readily decomposed into two volumes of hydrogen and one of oxygen.

331. Preparation of water. Water may be formed in four general ways:
(1) By the direct union of oxygen and hydrogen:

$$2 H_2 + O_2 = 2 H_2O.$$
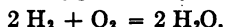
(2) By the union of free oxygen with hydrogen that is already in the combined condition:

$$2 O_2 + CH_4 = CO_2 + 2 H_2O.$$
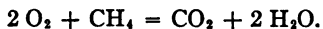
(3) By the union of free hydrogen with combined oxygen:

$$H_2 + CuO = H_2O + Cu.$$
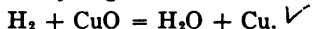
(4) By the union of combined oxygen with combined hydrogen:

$$MgO + 2 HCl = H_2O + MgCl_2.$$
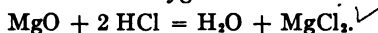
332. Burning of hydrogen. Hydrogen burns in air or in oxygen with the formation of water and the evolution of a large amount of energy in the form of heat. The water formed may be readily seen if the gases coming from the flame be conducted into some kind of a condenser where the steam will be changed to water (Fig. 61). Usually it is only necessary to place a beaker filled with cold water over the flame, and the steam will condense and appear as water on the bottom.

333. Oxyhydrogen blowpipe. A contrivance for utilizing this heat is shown in Fig. 62, and is known as the oxyhydrogen blowpipe. It consists of two concentric pipes. Oxygen issues from the inner and hydrogen from the outer.

Fig. 61

These gases mix only after leaving the blowpipe, and when ignited constitute the oxyhydrogen flame. This flame will readily melt platinum and is used in platinum works for that purpose.

Fig. 62

When the flame is directed against some infusible substance, such as lime or magnesia, it causes the latter to give out an intense white light, known as a lime-light, which is much used in stereopticons.
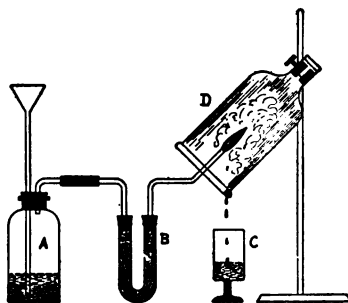
334. Burning of hydrogen compounds. Many combustible substances contain hydrogen, and when these burn the hydrogen is converted to water. Illuminating gas, kerosene, alcohol, and candle grease are examples of such substances. If a beaker filled with cold water be placed over any of these burning substances water will at once be seen collecting on the bottom (Fig. 63).

Marsh-gas, CH_4, may be considered as a typical combustible hydrogen compound. When it burns, the following reaction takes place:

$$CH_4 + 2 O_2 = CO_2 + 2 H_2O.$$

FIG. 63

335. The reduction of metallic oxides with hydrogen. Reduction.is the extraction of oxygen.

A **reducing agent** is any substance that can directly or indirectly bring about reduction.

Hydrogen is one of the best reducing agents. Many oxides of metals, when heated in an atmosphere of hydrogen, give up their oxygen to the hydrogen, forming water, and the metal is set free (Fig. 64):

$$CuO + H_2 = H_2O + Cu.$$
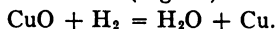
336. The action of a basic oxide on an acid. The oxides of most metals dissolve readily in acids with the formation of water and another compound known as a salt. The water is not visible in this case, because it remains mixed with the water that was already in the acid:

$$CuO + 2 HCl = H_2O + CuCl_2.$$

FIG. 64
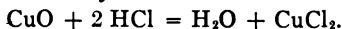
337. The quantitative composition of water. The reduction of metallic oxides with hydrogen gives a convenient method for determining the composition of water. It is only necessary to weigh the oxide before and after the reduction and also to weigh the water formed. The loss of weight of the oxide is evidently the oxygen that went to form the water, and the difference between the weight of the water and the loss of weight of the oxide is the weight of the hydrogen in the water.
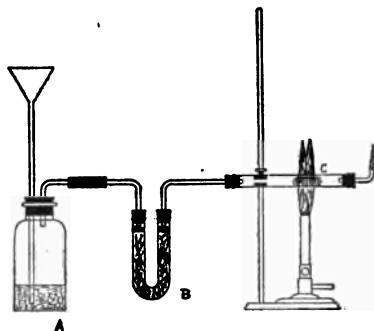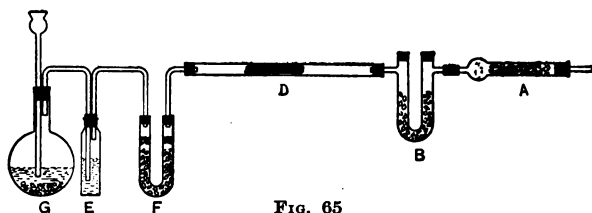
FIG. 65

A roll of copper-wire gauze which has been converted to oxide is weighed and placed in the tube D (Fig 65). An absorption U-tube and

prolong, B and A, are filled with granulated calcium chloride, a substance which has a great attraction for water. These are carefully weighed and connected by means of a rubber stopper to the end of the combustion-tube as shown.

The other end of the tube is then connected to a wash-bottle E, containing concentrated sulphuric acid, and a U-tube F, filled with calcium chloride, which in turn are connected to the outlet of a hydrogen generator G. A slow stream of hydrogen is then turned on.

A suitable burner is then placed under the tube and the flame turned on until reduction is complete. Care must be taken that the rubber stoppers are not burned, at the same time making sure that the glass tube is heated hot enough to prevent any condensation of water in the tube. When the reduction is complete the flame is removed and the hydrogen kept passing until the tube is cold. The copper is then weighed and also the two tubes containing the calcium chloride. The loss in weight of the copper oxide is the oxygen that went to form the water and the gain in weight of the calcium chloride tubes is the total water formed. The difference in the weight of the water and the oxygen is the hydrogen of the water.

The most careful experiments of this kind show that water contains 1 part of hydrogen by weight and 7.94 parts of oxygen by weight.

When water is decomposed it is found that 1 volume of oxygen exactly unites with 2 volumes of hydrogen, and that when the resulting pure gases are weighed it is found that 1 volume of oxygen weights 7.94 times as much as 2 volumes of hydrogen.

338. The purification of water.

(1) **Impurities in natural water.** Natural waters are subject to three kinds of impurities. As has already been mentioned, water is a great solvent and dissolves more or less of the substances with which it has been in contact. These include solids, liquids, and gases. If it has been in rapid motion, it will also contain quantities of finely divided material which it holds in suspension and which render it more or less muddy or opaque. Natural waters will also contain micro-organisms of animal or vegetable nature among which there may be disease-germs.
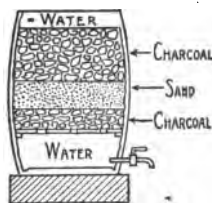
FIG. 66

(2) **Filtration** removes all of the insoluble particles and renders the water clear. But it should be remembered that all of the dissolved impurities and most of the disease-germs remain (Fig. 66).

(3) **Boiling the water** removes most of the dissolved gases and kills all of the germs. When the absolute purity of water for drinking purposes is uncertain or when it is known to be contaminated, it should invariably be boiled before using.

Fig. 67
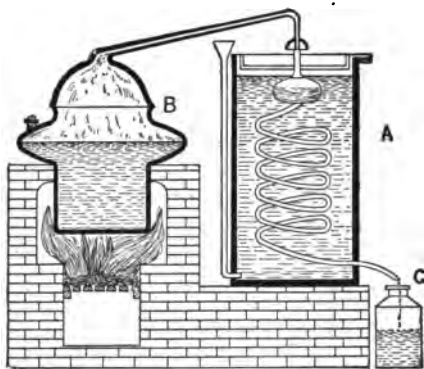
(4) **Distillation.** Water may be freed from all kinds of impurities by the process known as distillation. In this process the water is boiled and the steam passed through some kind of a condenser in which it is again converted to the liquid form. Of course if there are any volatile impurities they will pass over with the first portions of steam and be found in the distillate. If, however, the water was subjected to a preliminary boiling and the steam allowed to escape for some time, all of the volatile impurities would soon escape and then the rest could be distilled.

A common form of apparatus used in the distillation of water is shown in Fig. 67. *B* represents a copper retort or boiler; the steam then passes into a coil of tin pipe in *A*, where it is kept surrounded with cold water. The steam is condensed to water in this pipe and passes out as distilled water at *C*.
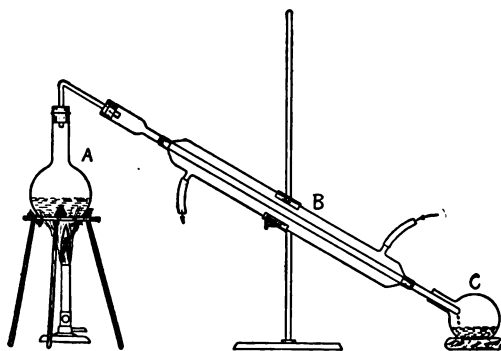
Fig. 68

(5) For laboratory purposes a form of condenser known as Liebig's condenser is much used. (Shown in Fig. 68.) It is

made entirely of glass with a removable inner tube. Water is kept circulating around the inner tube. It may be used for distilling many kinds of liquids besides water.

339. Uses. The uses of water are too numerous to mention, but its action in uniting with basic oxides to form bases and with acidic oxides to form acids should not be forgotten; nor its constant use as the medium in which many chemical reactions take place.

<div align="center">

Hydrogen Peroxide

</div>

340. Hydrogen peroxide is a thick, colorless, oily liquid.

Occurrence. Physical properties. It is found in minute quantities in snow and rain-water. As ordinarily prepared it is always formed in water solution. If the water be carefully evaporated, it may be obtained as a liquid. When perfectly pure this liquid has been obtained in a solid crystalline form which seems to be stable. If, however, it contains a trace of impurity, it is dangerously unstable and may explode with great violence. It dissolves in water in all proportions, in which solution it is constantly decomposing and giving off oxygen. It is commonly bought and sold in water solution containing about 3 per cent of hydrogen peroxide.

341. Chemical properties. On account of its instability and its constant tendency to separate into oxygen and water it is a powerful oxidizing agent. It readily oxidizes the hydrogen in hydrogen sulphide, setting the sulphur free:

$$H_2O_2 + H_2S = 2 H_2O + S.$$
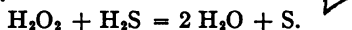
It instantly oxidizes black lead sulphide to white lead sulphate:

$$PbS + 4 H_2O_2 = PbSO_4 + 4 H_2O.$$

Many other sulphides behave in the same manner.

It readily liberates iodine from iodides in solution, with the formation of the corresponding hydroxide:

$$2 KI + H_2O_2 = 2 KOH + I_2.$$
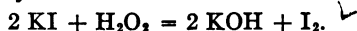
Toward many oxides and oxidizing agents it itself acts as a reducer. Thus with silver oxide it produces silver and oxygen:

$$H_2O_2 + Ag_2O = 2 Ag + H_2O + O_2.$$
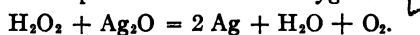
Manganese dioxide produces a rapid evolution of oxygen, becoming itself reduced to manganous oxide:

$$H_2O_2 + MnO_2 = H_2O + MnO + O_2.$$

Potassium permanganate solution in the presence of an acid is completely decolorized by hydrogen peroxide, with the evolution of oxygen.

342. Preparation. Hydrogen peroxide is commonly prepared by treating barium peroxide with sulphuric or hydrochloric acid. As the heat of the reaction is sufficient to decompose most of the hydrogen peroxide,

it is customary to keep the temperature down by the use of cracked ice
or snow:

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$
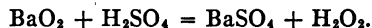
It is also formed in solution when a flame of burning hydrogen or illu-
minating gas is caused to impinge on the surface of water.

This is best done by causing the hydrogen to bubble up through the
water and igniting the bubbles as they burst on the surface.

When sodium peroxide is dissolved in water a solution of sodium hy-
droxide and hydrogen peroxide is formed:

$$Na_2O_2 + 2\,HOH = 2\,NaOH + H_2O_2.$$
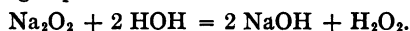
343. Uses. Hydrogen peroxide is of the greatest use in the laboratory
as an oxidizing agent. Unlike most other oxidizing agents, after it has
performed its work it leaves no undesirable impurity in the solution.
As an antiseptic in surgical operations it is invaluable, and it should re-
place the dangerous and inefficient carbolic acid so commonly used in
the household.

CHAPTER XXVI

The Halogens

Fluorine, F₂; Chlorine, Cl₂; Bromine, Br₂; Iodine, I₂.

These elements are classed together not only because they resemble each other in some of their properties as elements but because they unite with other elements forming compounds having similar properties. The hydrogen compound of each of these elements, when dissolved in water, has strongly acid properties.

The sodium compound of chlorine is common salt. Sodium bromide, iodide, and fluoride are compounds strongly resembling common salt; hence the name **halogen,** which means "salt-former."

Chlorine (Laboratory Exercise No. 15)

344. Appearance and occurrence. Chlorine is a heavy, greenish-yellow gas with a very disagreeable odor. It does not occur in the free condition, on account of its great tendency to enter into combination with other elements. It occurs in the combined condition in enormous quantities as sodium, potassium, and magnesium chlorides. Sodium chloride is the most abundant and forms about 3 per cent, by weight, of the sea-water. It is also found in the earth in the form of rock salt, especially in New York State, Michigan, West Virginia, Louisiana, Kansas, Utah, and California.

345. Physical properties. Its volume varies directly as its absolute temperature. That is, if the temperature be increased 1° C., the volume will increase 1/273 of the corresponding volume at 0° C. It is readily condensed to a light-yellow liquid by pressure and cold, and if the liquid be cooled sufficiently it solidifies to a light-yellow solid. The solid melts at − 102° C.; the liquid boils at − 33.6° C.

The critical temperature. of the gas is $+ 146°$. That is, above this temperature no amount of pressure will suffice to cause the gas to condense to a liquid.

Under normal conditions, at constant temperature, the volume of a body of chlorine varies inversely as the pressure.

It is soluble in water. One volume of water at ordinary temperature dissolves about two volumes of the gas. The solution is light-yellow.

The gas is diatomic; that is, it contains two atoms in the molecule, and its molecular formula is Cl_2.

A liter of the gas at normal temperature and pressure weighs 3.18 g.

Chlorine is about $2\frac{1}{2}$ times as heavy as air and 35.3 times as heavy as hydrogen.

Its molecular weight in grams occupies about 22.4 liters. This volume is known as the **gram-molecular volume** and is approximately a constant for all substances in the gaseous form. That is, a weight of a gas in grams equal to the molecular weight of the substance occupies 22.4 liters.

346. Chemical properties. Chlorine does not burn in the air, for the reason that it does not combine directly with oxygen. It does, however, support the combustion of a great many substances, especially the metals, which either burst into flame spontaneously when introduced into the gas in the finely divided condition or continue to burn with great violence when once ignited and thrust into the gas.

Phosphorus, finely divided antimony, and copper foil ignite when introduced into chlorine, forming the corresponding chlorides:

$$2\,P + 3\,Cl_2 = 2\,PCl_3.$$
$$2\,Sb + 3\,Cl_2 = 2\,SbCl_3.$$
$$Cu + Cl_2 = CuCl_2.$$
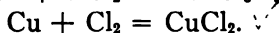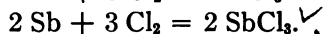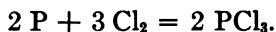
Chlorine has a great attraction for hydrogen. Equal volumes of hydrogen and chlorine explode with great violence, when the mixture is exposed to direct sunlight or the light from burning magnesium, forming two volumes of hydrogen chloride gas.

A solution of chlorine in water is rapidly changed by the

action of light into a very dilute solution of hydrochloric acid, oxygen gas being given off:

$$2 Cl_2 + 2 H_2O = 4 HCl + O_2.$$
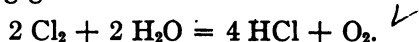
A jet of hydrogen gas will burn in an atmosphere of chlorine, or a jet of chlorine will burn in an atmosphere of hydrogen, forming hydrogen chloride.

Substances rich in hydrogen, if ignited and lowered into chlorine, continue to burn. A burning candle or a jet of illuminating gas burns with the formation of hydrogen chloride and voluminous clouds of lampblack:

$$C_2H_2 + Cl_2 = 2 HCl + 2 C.$$
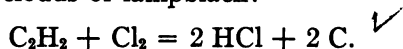
347. Test for an element. A test for an element is a process which causes that element, if present, to exhibit some characteristic property.

A single test is often not conclusive, and other tests should always be made when possible.

Test for free chlorine. The gas or liquid is added to a solution of potassium iodide and starch paste. The chlorine sets iodine free from the potassium iodide and this turns the starch blue.

Test for combined chlorine in the form of chloride. Silver nitrate added to the solution gives a white, curdy precipitate of silver chloride insoluble in nitric acid and soluble in ammonia.

348. Preparation. Chlorine is an extremely poisonous gas. Inhaled in a nearly pure condition, it would undoubtedly produce death. All experiments with it, as well as its preparation, should be carried on in a well-ventilated gas chamber. It is a very good plan to conduct all of these experiments on as small a scale as possible.

The gas is readily prepared by removing the hydrogen from hydrochloric acid. This can be accomplished by almost any oxidizing agent:

$$O + 2 HCl = H_2O + Cl_2.$$
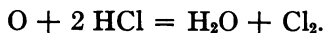
(1) **Laboratory method.** The oxidizing agent commonly used in the laboratory is manganese dioxide, MnO_2:

$$MnO_2 = MnO + O.$$
$$O + 2\,HCl = H_2O + Cl_2.$$
$$MnO + 2\,HCl = MnCl_2 + H_2O.$$
$$\overline{MnO_2 + 4\,HCl = MnCl_2 + 2\,H_2O + Cl_2.}$$
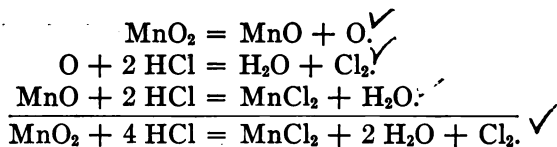
The manganese dioxide in lumps is placed in a flask A. This is covered with concentrated hydrochloric acid. The gas is passed through water in a bottle B (Fig. 69), to remove free HCl, and collected by downward displacement in bottle C. The color of the gas shows when the receiver is filled. A very small amount of heat is necessary.
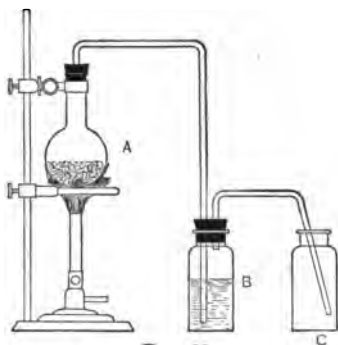
FIG. 69

If a slow stream of chlorine lasting for a long time is desired, it is better to put common salt in the bottom of the flask, cover this with a layer of manganese dioxide, and then add sulphuric acid.

The sulphuric acid acting on the salt gives hydrochloric acid, which in passing through the manganese dioxide gives up its hydrogen and the chlorine is set free. Any chloride with an oxidizing agent and sulphuric acid would act in the same way:

$$2\,NaCl + 2\,H_2SO_4 = 2\,HNaSO_4 + 2\,HCl.$$
$$MnO_2 = MnO + O.$$
$$O + 2\,HCl = H_2O + Cl_2.$$
$$MnO + H_2SO_4 = MnSO_4 + H_2O.$$
$$\overline{MnO_2 + 3\,H_2SO_4 + 2\,NaCl = MnSO_4 + 2\,HNaSO_4 + Cl_2}$$
$$+ 2\,H_2O.$$
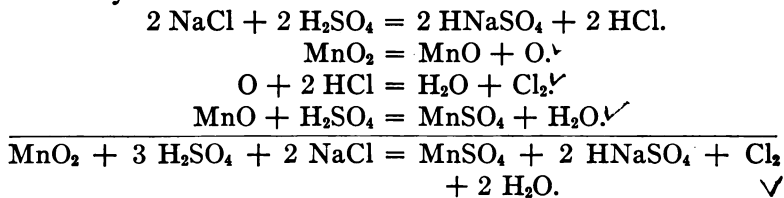
Where sulphuric acid is in excess with a univalent metal like sodium, the acid salt of sodium is always formed.

(2) **Method of manufacture.** Chlorine is made in large quantity by the electrolysis of sodium chloride, either melted or in solution. It is also made by **Deacon's process**, which consists in passing a mixture of HCl and air over bricks soaked in

copper sulphate and heated to a temperature of 380°. The copper sulphate acts as a catalytic agent. That is, it aids the reaction without becoming changed itself.

(3) **Other methods.** Chlorine may also be prepared by adding an acid to bleaching-powder:

$$CaOCl_2 + 2\,HCl = CaCl_2 + H_2O + Cl_2.$$
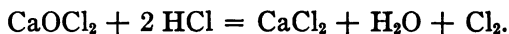
349. Uses.

(1) **Bleaching.** Chlorine is much used as a bleaching agent in the manufacture of paper from rags, also for bleaching cotton cloth.

This bleaching action takes place only in the presence of water:

$$Cl_2 + H_2O = 2\,HCl + O.$$
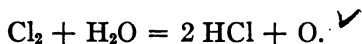
The chlorine combines with the hydrogen of the water, and the oxygen is at once available for oxidizing purposes. The reaction does not proceed far, however, unless there is something present for
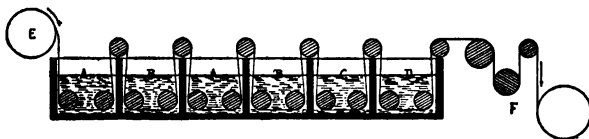
Fig. 70

the oxygen to combine with. An element which at once enters into a new combination the moment it is liberated is said to act in the **nascent condition.**

Chlorine bleaches, therefore, largely because it oxidizes and destroys the coloring matter (Fig. 70).

(2) **As a disinfectant.** Chloride of lime, when exposed to the air, slowly combines with carbon dioxide, forming calcium carbonate, gradually liberating chlorine, which destroys disagreeable odors and undesirable germs.

(3) It is also used very extensively in the manufacture of a large variety of organic compounds, such as chloroform, $CHCl_3$; ethyl chloride, C_2H_5Cl; methyl chloride, CH_3Cl; and carbon tetrachloride, CCl_4.

350. Common compounds. **Hydrogen chloride** and the chlorides of the metals known as salts. **Chlorates,** salts of chloric acid, $HClO_3$, and **perchlorates,** salts of perchloric acid, $HClO_4$. The

oxides, Cl_2O, ClO_2, and Cl_2O_7. **Chloroform, $CHCl_3$, and carbon tetrachloride, CCl_4.**

Hydrogen Chloride and Hydrochloric Acid (Laboratory Exercise No. 16)

351. Appearance and occurrence. Hydrogen chloride is a colorless gas, with a suffocating odor and a sour taste, which occurs in nature in volcanic gases, and rivers and springs that have their origin in volcanic regions. It constitutes an essential ingredient of the juices of the stomach.

352. Physical properties. Under normal conditions the gas obeys Boyle's and Charles's laws. When subjected to pressure and cold it condenses to a colorless liquid which, on further cooling, changes to a crystalline solid. The solid melts at $-112°$ and the liquid boils at $-83°$.

Its critical temperature is $52°$, and its critical pressure 86 atmospheres. (One atmosphere is about 15 lbs. per square inch.)

It has an enormous attraction for water, so much so that it causes the moisture to condense from the air, forming a cloud. This cloud consists of minute globules of hydrochloric acid solution.

One volume of water at $0°$ dissolves 500 volumes of the gas, with the evolution of much heat. This solution constitutes the hydrochloric acid of the laboratory.

A gram-molecular weight of the gas occupies 22.4 liters.

353. Chemical properties. The dry gas or the anhydrous liquid has no acid properties. The water solution, however, shows all the usual properties common to acids. Here, again, the water plays the part of a catalytic agent. The solution reacts with metals to form salts, with the evolution of hydrogen; with basic oxides and bases, forming salts and water; and with carbonates, forming salts, water, and carbon dioxide.

Hydrochloric acid, or **muriatic acid,** is a water solution of hydrogen chloride gas, having a specific gravity of 1.19 and containing about 38 per cent HCl.

If any mixture of water and hydrogen chloride be boiled, the compound which is present in excess, either the water or

the HCl, will first escape, until the remaining liquid contains about 20 per cent of the dissolved gas. The concentration will then remain constant during further evaporation.

Hydrochloric acid is a good conductor of electricity. When the current is passed through it equal volumes of hydrogen and chlorine are obtained.

Oxidizing agents readily decompose it, setting chlorine free:

$$2 \, KMnO_4 = K_2O + 2 \, MnO + 5 \, O.$$
$$5 \, O + 10 \, HCl = 5 \, H_2O + 5 \, Cl_2.$$
$$K_2O + 2 \, HCl = 2 \, KCl + H_2O.$$
$$2 \, MnO + 4 \, HCl = 2 \, MnCl_2 + 2 \, H_2O.$$
$$\overline{2 \, KMnO_4 + 16 \, HCl = 2 \, KCl + 2 \, MnCl_2 + 8 \, H_2O + 5 \, Cl_2.}$$
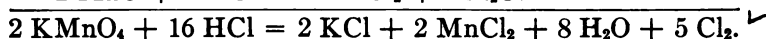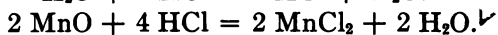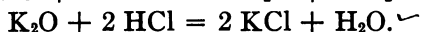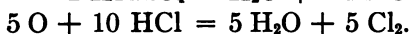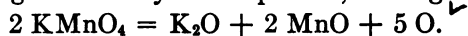
Silver nitrate gives a heavy, white, curdy precipitate of silver chloride, insoluble in nitric acid and soluble in ammonia:

$$HCl + AgNO_3 = AgCl + HNO_3.$$
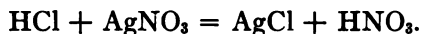
Hydrogen chloride gas unites directly with ammonia gas, NH_3, to form solid, white ammonium chloride.

$$HCl + NH_3 = NH_4Cl.$$

The white cloud so commonly seen hovering about the re-agent bottles is ammonium chloride, formed by the meeting of HCl gas from the hydrochloric acid bottle and ammonia from the ammonium hydroxide bottle.

354. Preparation. Volatile and stable acids may usually be made by treating their salts with a less volatile acid. Sulphuric acid is very stable and boils at a very high temperature. When it is mixed with a salt of almost any other acid it forms a sulphate and the other acid is set free.

FIG. 71

(1) **Laboratory method.** One molecular weight of common salt, NaCl, moistened with water, is treated with one molecular weight of concentrated sulphuric
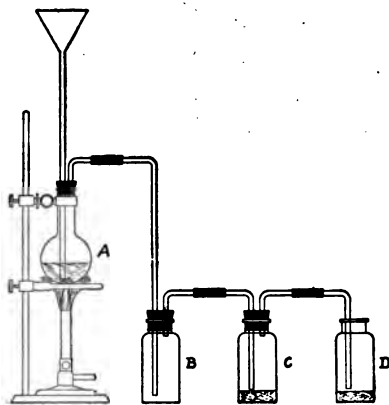
acid in the flask A, as indicated in Fig. 71. The evolved gas is passed through the bottle B, which is used as a receiving bottle for the gas. The bottle C contains a little water for forming a solution of the gas. The tube in this bottle should not quite touch the surface of the water. The bottle D contains some strong ammonium hydroxide to absorb any unused HCl. Several bottles may be filled at B by upward displacement, as the gas is heavier than air.

The residue left in the flask A is acid sodium sulphate, $HNaSO_4$:

$$NaCl + H_2SO_4 = HNaSO_4 + HCl.$$
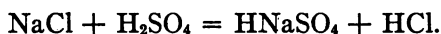
A much higher temperature and more salt would be necessary to form the normal salt, Na_2SO_4.

(2) **From the solution.** A good method for obtaining a supply of HCl gas is to arrange a flask of concentrated hydrochloric acid as shown in Fig. 72, with a small separatory funnel provided with a long tube and stopcock. The funnel is filled with concentrated sulphuric acid, and this is allowed to fall drop by drop into the hydrochloric acid. The addition of each drop causes a voluminous evolution of HCl gas. The gas is dried by passing through a bottle containing sulphuric acid.
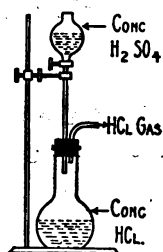
(3) **Method of manufacture.** Hydrochloric acid is made on the large scale also by treating sodium chloride with sulphuric acid and causing the gas to ascend through towers filled with coke over which water is constantly running. The water absorbs the acid gas and a strong solution of the gas in water issues from the bottom of the tower. This solution constitutes the common hydrochloric, or **muriatic,** acid of commerce. It is colored slightly yellow by iron, which is present in the form of ferric chloride.

FIG. 72

The chemical action takes place in two steps:

First, at comparatively low temperature, hydrogen chloride and acid sodium sulphate are formed:

$$2\,NaCl + H_2SO_4 = HNaSO_4 + NaCl + HCl.$$

The solid residue from the first reaction is then heated to a

high temperature, and a second reaction takes place, forming the normal salt and more hydrogen chloride (Fig. 73):

$$HNaSO_4 + NaCl = Na_2SO_4 + HCl.$$
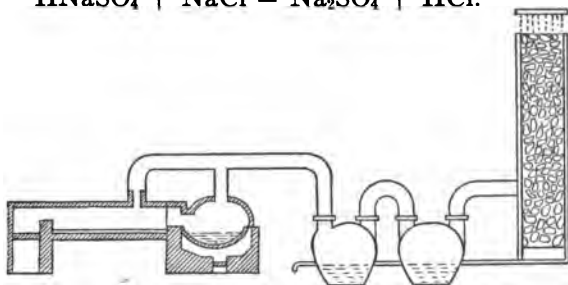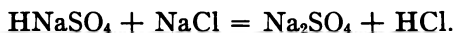
(4) **Other methods.** Hydrogen chloride might also be made by the direct union of hydrogen and chlorine:

$$H_2 + Cl_2 = 2\,HCl.$$
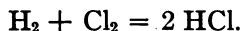
When chlorine acts as an oxidizing agent in the presence of water, hydrogen chloride is always produced:

$$3\,Cl_2 + 3\,H_2O = 6\,HCl + 3\,O.$$
$$2\,P + 3\,O = P_2O_3.$$
$$P_2O_3 + 3\,H_2O = 2\,H_3PO_3.$$
$$\overline{3\,Cl_2 + 6\,H_2O + 2\,P = 2\,H_3PO_3 + 6\,HCl.}$$
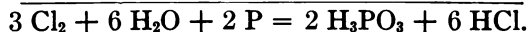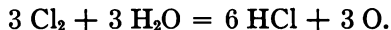
355. Uses. Hydrochloric acid is used for the preparation of chlorine and chlorides and for cleaning metals preparatory to tinning, galvanizing, or lacquering.

Bromine (Laboratory Exercise No. 17)

356. Appearance and occurrence. Bromine is a heavy, dark-red, volatile liquid with a very bad odor. In thin layers it is transparent. The water solution and vapor are both red.

It does not occur free, on account of its tendency to enter into combination with other substances. It is found chiefly as magnesium bromide, associated with salt deposits. Most of the bromine from this country comes from Michigan, Pennsylvania, and West Virginia.

357. Physical properties. The liquid is very volatile at ordinary temperatures, giving off a red gas which attacks the

mucous membranes of the eyes, nose, and throat. When
sufficiently cooled it solidifies to a red crystalline solid. The
solid melts at $-7.2°$ and the liquid boils at $59°$. 100 g. of
water dissolve about 3 g. of bromine. It is quite soluble in
carbon disulphide, alcohol, and ether.

If a solution of bromine in water be shaken with some solvent
which does not itself dissolve in the water, a large proportion of
the bromine will enter the solvent and color it yellow or red.

The vapor density of bromine is 79.96, its molecular weight
is therefore 159.9. Since the atomic weight is 79.96, the
formula for the gas is Br_2.

358. Chemical properties. Bromine does not burn or form
any oxides. **Hypobromous acid**, HBrO, and **bromic acid**, $HBrO_3$,
are known, however, and may be considered as compounds
of Br_2O and Br_2O_5 with water. In its chemical activities bro-
mine is similar to chlorine. It unites directly with many
metals to form bromides; and antimony and arsenic take fire
when placed in it. It unites directly with hydrogen to form
hydrogen bromide.

359. Test. When chlorine water is added to a solution of
a bromide, bromine is set free. The solution to be tested is
treated with chlorine water in a test-tube. A few cubic cen-
timeters of carbon disulphide are then added and the tube
well shaken. If any bromine is present the globule of carbon
disulphide will be turned yellow or red, according to the quan-
tity of bromine present.

360. Preparation.

(1) **Laboratory method.** Bromine is prepared in the labora-
tory by heating a bromide with sulphuric acid and an oxidiz-
ing agent. Manganese dioxide and potassium bromide are
commonly used. The manganese dioxide gives 1 atom of oxy-
gen for oxidizing purposes. This is equivalent to 2 bromines
or 2 potassium bromides. 1 sulphuric acid molecule is neces-
sary for the basic oxide of manganese, and 2 for the potassium,
to form the acid sulphate. The equation can now be written
at once:

$$2\,KBr + MnO_2 + 3\,H_2SO_4 = 2\,HKSO_4 + MnSO_4 + 2\,H_2O + Br_2.$$
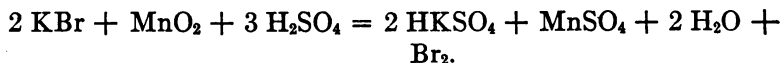
The bromine is best collected under water (Fig. 74).

(2) **Method of manufacture.** After the salt has been crystallized from water the bromine is left in the residual liquor (known as the mother liquor) as magnesium bromide. This liquor is treated with potassium chlorate and a small quantity of sulphuric acid and distilled:

FIG. 74

$$3 \text{ MgBr}_2 + \text{KClO}_3 + 3 \text{ H}_2\text{SO}_4 = 3 \text{ MgSO}_4 + \text{KCl} + 3 \text{ H}_2\text{O} + 3 \text{ Br}_2.$$
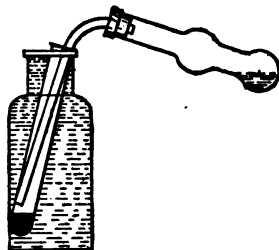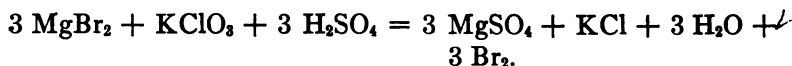
(3) **Other methods.** Hydrobromic acid could be oxidized, forming water and bromine:

$$2 \text{ HBr} + \text{O} = \text{H}_2\text{O} + \text{Br}_2.$$
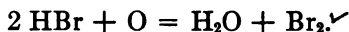
Chlorine sets bromine free from bromides:

$$\text{Cl}_2 + 2 \text{ KBr} = 2 \text{ KCl} + \text{Br}_2.$$
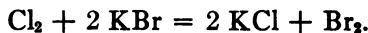
361. Uses. Bromine is valuable as an oxidizing agent in the laboratory:

$$\text{Br}_2 + \text{H}_2\text{O} = 2 \text{ HBr} + \text{O}.$$
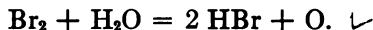
It is used also in the manufacture of hydrobromic acid, bromides, and aniline dyes.

Bromides of sodium, potassium, and ammonium are much used in medicine.

362. Common compounds. Hydrobromic acid, HBr; potassium, sodium, and **ammonium** bromides.

Hydrogen Bromide, Hydrobromic Acid

363. Physical properties. Hydrogen bromide is a colorless gas resembling hydrogen chloride. The gas obeys Boyle's and Charles's laws. If it be sufficiently cooled, it condenses to a colorless liquid, and this, on further cooling, to a white solid.

The gas has a great attraction for water and fumes strongly in moist air, because it causes the moisture to condense in the form of a cloud, consisting of minute globules of hydrobromic acid solution.

One volume of water dissolves 600 volumes of the gas. This solution constitutes the hydrobromic acid of the laboratory. Its gas density is 40.48; its molecular weight is therefore 80.96. 1 liter of the gas weighs 3.61 g. 1 gram-molecular weight occupies 22.4 liters.

364. Chemical properties. The dry gas is very similar to hydrogen chloride. It virtually has no acid properties. It does not burn or support combustion. It is not quite as stable as hydrogen chloride.

The water solution known as hydrobromic acid is an active acid similar to hydrochloric acid. It reacts with metals, forming bromides and setting hydrogen free; with basic oxides and bases, forming bromides and water. Almost any oxidizing agent will transform its hydrogen into water and set the bromine free. The gas reacts with ammonia gas to form clouds of solid ammonium bromide, and its solution gives a heavy cream-colored precipitate with silver nitrate.

365. Test. Its acid reaction toward litmus paper and metals, and the copious evolution of bromine when treated with an oxidizing agent, constitute a sufficient test for it.

366. Preparation. Hydrobromic acid is most conveniently made by using bromine as an oxidizing agent. If bromine is allowed to come in contact with moist red phosphorus, the phosphorus is oxidized to phosphorous or phosphoric acid, and all of the bromine is transformed to hydrobromic acid.
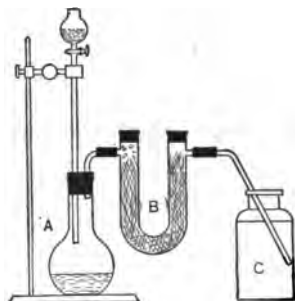
Red phosphorus and water are placed in a flask A, and bromine is allowed to flow in drop by drop from a suitable funnel. The escaping gas is caused to pass through a tube B, filled with red phosphorus, to absorb any bromine that might be carried over with the hydrogen bromide, and is then absorbed in water, if necessary, to form the solution:

$$3 \text{ Br}_2 + 3 \text{ H}_2\text{O} = 6 \text{ HBr} + 3 \text{ O}.$$
$$2 \text{ P} + 3 \text{ O} = \text{P}_2\text{O}_3.$$
$$\text{P}_2\text{O}_3 + 3 \text{ H}_2\text{O} = 2 \text{ H}_3\text{PO}_3.$$
$$\overline{3 \text{ Br}_2 + 2 \text{ P} + 6 \text{ H}_2\text{O} = 2 \text{ H}_3\text{PO}_3 + 6 \text{ HBr}.}$$

FIG. 75
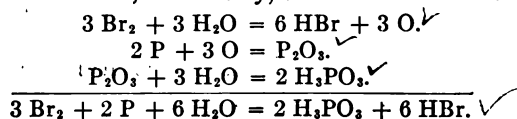
Iodine (Laboratory Exercise No. 17)

367. Appearance and occurrence. Iodine is a gray-black crystalline solid. It does not occur in the free condition, but is found in many sea-plants and as sodium iodate, $NaIO_3$, in the mother liquors from which sodium nitrate has been crystallized in Chili. Most of the world's supply comes from this source.

368. Physical properties. At ordinary temperatures it evaporates completely when exposed to the air. A large flask containing free iodine shows a distinct violet color, due to the vapor of iodine.

When heated, iodine melts to a black liquid at 114° and boils at 184°. During the melting it evolves quantities of violet-colored vapor. The vapor, if slowly cooled, condenses at once to the crystalline form. In other words, iodine sub-limes readily.

It is very slightly soluble in water, coloring the solution brown. It is quite soluble in alcohol, giving a brown solution which is known as **tincture of iodine**. Carbon disulphide dissolves it very readily, dilute solutions having a purple color similar to that of iodine vapor. The best solvent, however, for iodine is a solution of potassium iodide. The solvent action is due to the fact that a very soluble compound of iodine with the iodide is formed.

The density of iodine vapor above the boiling-point gives a molecular weight of 254.8; since the atomic weight is 126.97, the molecule of iodine must contain 2 atoms. Iodine is volatile with steam; that is, if water containing either dissolved or suspended iodine be boiled, the iodine all passes off with the steam.

369. Chemical properties. Iodine does not burn in oxygen, but when treated with oxidizing agents it is oxidized to iodic acid, HIO_3. If this compound be heated, water splits off and leaves iodine pentoxide, I_2O_5, a white amorphous powder:

$$10\ HNO_3 = 5\ H_2O + 10\ NO + 15\ O.$$
$$15\ O + 3\ I_2 = 3\ I_2O_5.$$
$$\underline{3\ I_2O_5 + 3\ H_2O = 6\ HIO_3.}$$
$$10\ HNO_3 + 3\ I_2 = 6\ HIO_3 + 10\ NO + 2\ H_2O.$$
$$2\ HIO_3\ \text{heated} = I_2O_5 + H_2O.$$
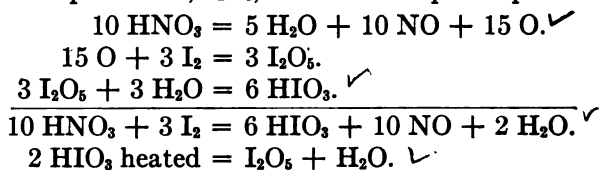
I_2O_5 is the anhydride of iodic acid.

Iodine in the presence of water and an oxidizable substance acts as an oxidizing agent:

$$I_2 + H_2O = 2\ HI + O.$$
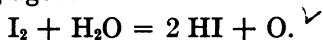
If hydrogen sulphide be passed through some water containing pulverized iodine, the hydrogen is removed from the H_2S, forming hydrogen iodide, which remains in solution, and sulphur is precipitated. The sulphur may be filtered off and a solution of **hydrogen iodide** obtained:

$$I_2 + H_2O = 2\ HI + O.$$
$$O + H_2S = H_2O + S.$$
$$\overline{I_2 + H_2S = 2\ HI + S.}$$
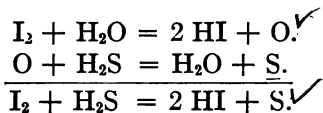
When iodine is used as an oxidizing agent in the presence of water, hydrogen iodide is formed. This has just been illustrated by the action of iodine on hydrogen sulphide.

Iodine and iodine solutions color the skin brown. These brown stains may be removed readily with ammonium hydroxide.

If chlorine water be added little by little to a very small quantity of potassium iodide solution, until a great excess is present, the following changes will be noticed:

The first few drops liberate iodine, which is at once dissolved in the potassium iodide solution, coloring it yellow or red:

$$Cl_2 + 2\ KI = 2\ KCl + I_2.$$
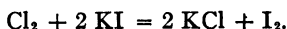
On the further addition, so much of the KI is decomposed that there is not enough present to hold the iodine in solution, and a black precipitate of iodine is formed. The further addition of chlorine causes the iodine to dissolve to a colorless solution.

This is because the chlorine, acting as an oxidizing agent, oxidizes the iodine to iodic acid.

$$5\ Cl_2 + 5\ H_2O = 10\ HCl + 5\ O.$$
$$I_2 + 5\ O = I_2O_5.$$
$$\underline{I_2O_5 + H_2O = 2\ HIO_3.}$$
$$\overline{5\ Cl_2 + 6\ H_2O + I_2 = 2\ HIO_3 + 10\ HCl.}$$
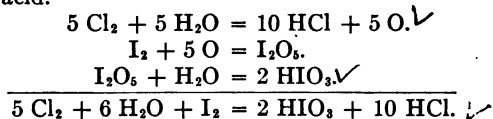
370. Test for iodine. If a water solution of free iodine be shaken with a little carbon disulphide, chloroform, or ether—liquids which do not dissolve in water but are good solvents of iodine—the iodine will be concentrated in the carbon disulphide and color it purple.

Also, if a small quantity of cooked starch solution be added to the solution containing iodine, a deep-blue color will be produced.

To test for iodine in the form of iodide, some starch solution is first added, and then a little of some oxidizing agent which will set the iodine free. A small quantity of chlorine water is commonly used. If any iodide is present, the liberated iodine will color the starch solution blue.

371. Preparation.

(1) **Laboratory method.** In the laboratory iodine is usually prepared by oxidizing potassium iodide in the presence of an acid. Almost any oxidizing agent will suffice.

Any iodide treated with manganese dioxide and sulphuric acid gives iodine:

$$MnO_2 = MnO + O.$$
$$O + 2 KI = K_2O + I_2.$$
$$MnO + H_2SO_4 = MnSO_4 + H_2O.$$
$$K_2O + 2 H_2SO_4 = 2 HKSO_4 + H_2O.$$
$$\overline{2 KI + MnO_2 + 3 H_2SO_4 = MnSO_4 + 2 HKSO_4 + 2 H_2O + I_2.}$$
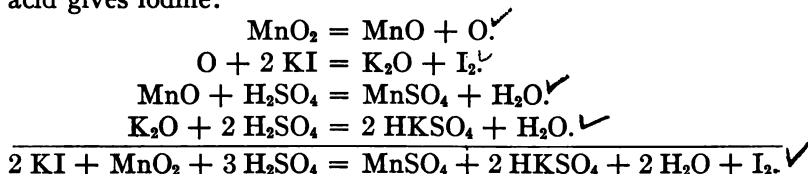
A small quantity of the mixture is placed in a test-tube with a few drops of water. The tube is fitted with a cork stopper and short, straight glass delivery-tube. Over this tube another test-tube is placed loosely. When the mixture is heated the iodine rapidly distils over and condenses in the receiving-tube (Fig. 76).
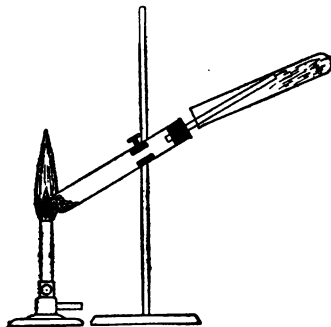
(2) **Technical method.** Since iodine is originally obtained as sodium iodate, $NaIO_3$, the iodine is already in a high stage of oxidation; hence oxidizing agents would have no effect. The $NaIO_3$ must therefore be treated with reducing agents —that is, it must itself act as an oxidizing agent.

FIG. 76

The sodium iodate is commonly treated with a mixture of monosodium and disodium sulphites. The iodine is set free and the two sulphites changed to sulphates. The following reactions will make this clear:

$$2 NaIO_3 = Na_2O + I_2O_5.$$
$$I_2O_5 = I_2 + 5 O.$$
$$3 Na_2SO_3 + 3 O = 3 Na_2SO_4.$$
$$2 HNaSO_3 + 2 O = 2 HNaSO_4.$$
$$2 HNaSO_4 + Na_2O = 2 Na_2SO_4 + H_2O.$$
$$\overline{2 NaIO_3 + 3 Na_2SO_3 + 2 HNaSO_3 = 5 Na_2SO_4 + I_2 + H_2O.}$$
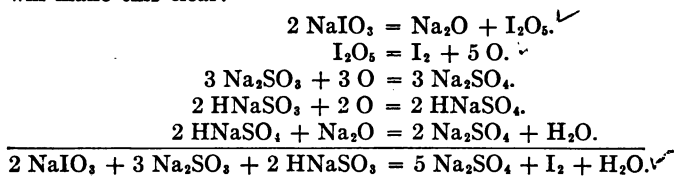
The crude iodine is purified by sublimation (Fig. 77).

(3) **Other methods.** Chlorine and bromine both liberate iodine from iodides:

$$Cl_2 + 2 KI = 2 KCl + I_2.$$
$$Br_2 + 2 KI = 2 KBr + I_2.$$
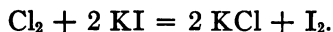
Iodine could also be set free by electrolyzing a solution of an iodide.

. 372. **Uses.** Tincture of iodine is much used for reducing bruises and sprains. Potassium iodide is used as a medicine, and iodine is used in the manufacture of many aniline dyes.
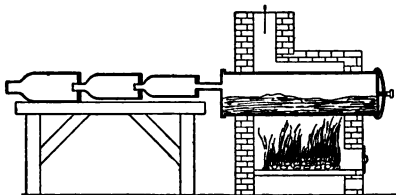
373. **Common compounds.** Hydrogen iodide, HI, a solution of which in water is called hydroiodic acid; potassium iodide, KI; potassium iodate, KIO_3; and hydrogen iodate, HIO_3, or iodic acid.

FIG. 77

Hydrogen Iodide and Hydroiodic Acid

374. **Physical properties.** Hydrogen iodide is a heavy, colorless gas with a sharp odor. The gas has a strong attraction for water, so that it fumes in moist air, just as hydrogen chloride and hydrogen bromide do. It is extremely soluble in water: 1 volume of water at 0° dissolves about 1,500 volumes of the gas, forming a strong solution having acid properties. This solution is known as hydroiodic acid.

One gram-molecule of the gas occupies 22.4 liters at normal temperature and pressure. Dividing 128 g. by 22.4 gives 5.71 g. as the weight of a liter.

375. **Chemical properties.** The gas is rather unstable and breaks up into hydrogen and iodine when heated. For this reason it is an excellent reducing agent. If a jar of the gas be poured on a Bunsen flame, the hydrogen burns and a cloud of purple iodine vapor is set free.

The water solution has properties very similar to a solution of hydrogen chloride or hydrogen bromide.

376. **Preparation.** The gas is best prepared by allowing iodine in potassium iodide solution to drop on moist red phosphorus.

The escaping gas is passed through a tube filled with red phosphorus to remove any traces of iodine vapor (Fig. 78).

It may be assumed that phosphorus tri-
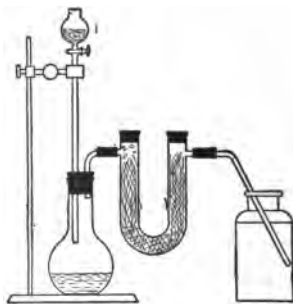
FIG. 78

iodide is first formed and that this compound reacts with the water to form phosphorous acid and hydrogen iodide:

$$2 P + 3 I_2 = 2 PI_3.$$
$$2 PI_3 + 6 H_2O = 2 H_3PO_3 + 6 HI.$$
$$2 P + 3 I_2 + 6 H_2O = 2 H_3PO_3 + 6 HI.$$
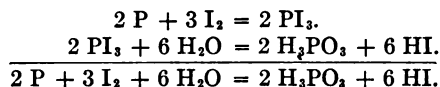
The gas cannot be made by the action of sulphuric acid on an iodide, for the reason that it is such a strong reducing agent that it reduces some of the sulphuric acid, and the product is contaminated with hydrogen sulphide, sulphur dioxide, and iodine.

Fluorine

377. Occurrence and physical properties. Fluorine is a pale-yellow gas similar to chlorine. It does not occur in the free condition, but is found combined in many rocks and minerals, especially **calcium fluoride**, CaF_2, and **cryolite**, $AlF_3 \cdot 3NaF$. The molecular weight obtained from its gas density is 38. Since its atomic weight is 19, the molecule has two atoms, F_2.

The gas can be liquefied by pressure and cold.

378. Chemical properties. The gas combines energetically with every element except oxygen. Many solid elements in the form of powder burst into flame when placed in the gas. Powdered silicon becomes silicon tetrafluoride. Fluorine extracts the hydrogen from water and hydrochloric acid.

379. Test for fluorine. To test for the presence of fluorine, the substance is pulverized and mixed with concentrated sulphuric acid in a small lead dish. Over this is placed a piece of glass covered with beeswax on which some definite markings have been made. If any fluoride is present, sufficient hydrogen fluoride will be formed to etch the glass, the etching, however slight, being readily visible after the wax has been removed.

380. Preparation. Fluorine cannot be made by oxidizing hydrofluoric acid in the same way that chlorine, bromine, and iodine may be prepared. It has been prepared, however, by electrolyzing liquid hydrogen fluoride at low temperature (Fig. 79).
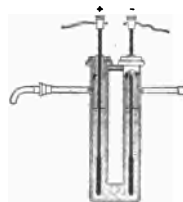
FIG. 79

381. Common compounds. Calcium fluoride, or **fluorite**, CaF_2; **cryolite**, $AlF_3 \cdot 3NaF$; hydrogen fluoride, HF; silicon tetrafluoride, SiF_4; and hydrofluosilicic acid, H_2SiF_6.

Hydrogen Fluoride and Hydrofluoric Acid

382. Physical properties. Hydrogen fluoride, below the temperature of 19.4°, is a colorless liquid, but, at the temperature at which it is commonly made, it is a colorless gas similar to hydrogen chloride. Liquid hydrogen fluoride boils at 19.4°. It mixes with water forming a solution having all the usual properties of an acid and known as hydrofluoric acid. Hydrogen fluoride gas fumes in moist air. The gas density below 30° indicates a molecular weight of 40; the formula must therefore be H_2F_2. As the temperature increases the density falls, until the temperature 88° is reached, when it becomes 10. This corresponds to the formula HF. When two or more molecules of a substance unite to form a molecule having the same chemical composition, the substance is said to **polymerize**. The process is called **polymerization** and the new substance is said to be a **polymer** of the old.

383. Chemical properties. Hydrogen fluoride is an extremely stable compound and cannot easily be separated into hydrogen and fluorine. No oxidizing agent decomposes it, as it does the other halogen acids. The water solution has all the usual properties characteristic of acids.

This solution reacts with many metals, forming fluorides and hydrogen, with basic oxides and hydroxides to form fluorides and water, and it decomposes carbonates.

Besides these properties it has the unusual property of transforming the silicon of sand and silicates into silicon tetrafluoride, SiF_4, a gas:

$$4\,HF + SiO_2 = SiF_4 + 2\,H_2O.$$
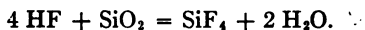
Glass, which is a mixture of certain silicates, is rapidly cut or etched by either the gas or the solution. The gas produces a white etching and the liquid deep, smooth cuts. In order to etch glass with hydrofluoric acid, the object to be etched is first covered with a thin coating of wax or paraffine, the design is then drawn on the paraffined surface with a sharp point, and the surface is exposed to the action of the gas or washed over with a strong solution of the acid:

$$CaSiO_3 + 6\,HF = CaF_2 + SiF_4 + 3\,H_2O.$$

The acid does not attack gold, platinum, or paraffine, and is commonly kept in paraffine bottles.

384. Preparation. Hydrogen fluoride is usually made by the action of sulphuric acid on pulverized calcium fluoride:

$$CaF_2 + H_2SO_4 = CaSO_4 + H_2F_2.$$
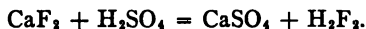
The gas is condensed in water and later purified if necessary by distillation. The process is carried out in a lead or platinum retort.

It could also be made by heating acid potassium fluoride:

$$2 \text{ HKF}_2 \text{ heated } = 2 \text{ KF} + \text{H}_2\text{F}_2.$$
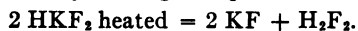
And by the direct union of hydrogen and fluorine:

$$\text{H}_2 + \text{F}_2 = \text{H}_2\text{F}_2.$$
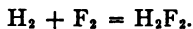
385. **Uses.** The solution is much used in the laboratory for decomposing silicates and for etching chemical glassware. It is also used for cleaning sand from iron castings.

CHAPTER XXVII

SULPHUR AND HYDROGEN SULPHIDE

Sulphur (Laboratory Exercise No. 18)

386. Appearance and occurrence. Sulphur is a yellow crystalline solid that may exist in several different forms. It occurs in the free condition in large quantities in volcanic regions, especially in Sicily, Mexico, and the United States. It is found in enormous quantities as sulphides and sulphates. Some of the natural compounds of it in the form of sulphides are: **iron pyrites,** FeS_2; **galena,** PbS; **stibnite,** Sb_2S_3; **copper pyrite,** $CuFeS_2$; and in the form of sulphates: **gypsum,** $CaSO_4 + 2 H_2O$; **barite,** $BaSO_4$, commonly called **barytes;** and **celestite,** $SrSO_4$.

387. Physical properties. Sulphur may exist in several allotropic modifications, the three most important of which are the **rhombic, prismatic,** and **plastic** varieties.

(1) **Rhombic sulphur.** This is the common form in which sulphur is found in the native condition and the form to which the other two varieties revert on standing. It is perfectly transparent, has a specific gravity of 2.06, and melts at 114.5°. When very slowly heated it melts to a thin straw-colored liquid. Further heating causes it to become dark-red in color and so thick that it will hardly flow. As the temperature becomes higher it again gets thin, but retains the dark color and finally boils at a temperature of 448.5°. On cooling it goes through the reverse changes.

The density of sulphur vapor varies according to the temperature, indicating molecular weights corresponding to the formulas S_8, S_6, S_4, and S_2. The larger molecules are found in the vapor at low temperatures and the small ones at high temperatures.

This variety of sulphur is slightly soluble in alcohol and

ether and quite soluble in carbon disulphide. If a carbon disulphide solution be allowed to evaporate slowly, almost perfect crystals of the rhombic variety are formed (Fig. 80).

(2) **Prismatic, or mono-clinic, sulphur.** If a large mass of sulphur be melted and allowed to cool slowly until a crust has formed, and the remaining liquid be poured out through a hole in the crust, the whole interior of the vessel will be filled with long, needle-like crystals (Fig. 81). These belong to the mono-clinic variety.

FIG. 80

They are perfectly transparent, have a specific gravity of 1.96, and melt at 119° C. On standing, however, they soon become opaque, for the reason that the large crystals turn into a mass of small crystals of the rhombic variety.

FIG. 81

(3) **Plastic sulphur.** If a thin stream of melted sulphur almost in the viscous condition be poured into cold water, the molecules do not have time to arrange themselves in a crystalline form and the result is a transparent, amorphous, elastic mass almost resembling rubber or gum. This is known as **plastic sulphur** and is insoluble in carbon disulphide. On standing several days it becomes hard and is found to contain a large quantity of crystals of the rhombic variety.

388. Chemical properties. Sulphur burns readily in air and in oxygen, giving a light-blue flame and a light-white smoke. The product is mostly sulphur dioxide, SO_2, a colorless gas, and some sulphur trioxide, SO_3, a white solid. The presence of some sulphur trioxide undoubtedly accounts for the white appearance of the gas.

$$S + O_2 = SO_2.$$
$$2 S + 3 O_2 = 2 SO_3.$$
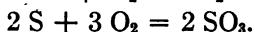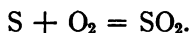
These oxides are both acidic and unite with water to form acids.

$SO_2 + H_2O = H_2SO_3$, hydrogen sulphite, or sulphurous acid.
$SO_3 + H_2O = H_2SO_4$, hydrogen sulphate, or sulphuric acid.
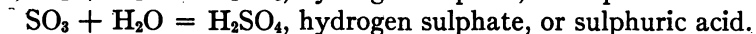
Sulphur vapor unites directly with hydrogen to form hydrogen sulphide gas:

$$S_2 + 2 H_2 = 2 H_2S.$$
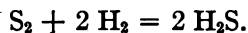
Moist sulphur, as well as sulphur at high temperatures, unites directly with many metals to form sulphides:

$$Fe + S = FeS.$$
$$Cu + S = CuS.$$
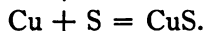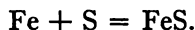
The element has three different valences, 2, 4, and 6, as shown by the compounds H_2S, SO_2, and SO_3.
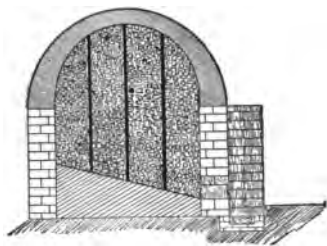
Fig. 82

389. Test. Free sulphur may be detected by heating the substance in contact with a bright surface of silver or copper. If any sulphur is present, a black spot of the sulphide of the metal will be formed. If it is in a compound, a small portion should be pulverized and mixed with sodium carbonate. This mixture is then heated on charcoal with the reducing flame of the blowpipe. The product is mixed with water and placed on bright silver or copper. A black spot will again show the presence of sulphur.

390. Extraction of sulphur. Sulphur is extracted from the earthy material with which it is mixed by simply heating the mass. The sulphur melts and runs out at the bottom. This is accomplished in two ways. Either the sulphur-bearing material is stacked in a pile and some of the sulphur allowed to burn (Fig. 82) and generate heat enough to melt the rest, or the sulphur ore is placed in retorts and the sulphur melted with superheated steam.

In Louisiana, artesian wells are sunk to the sulphur-bearing strata. The sulphur is melted with superheated steam and brought to the surface by means of water and compressed air (Fig. 83).
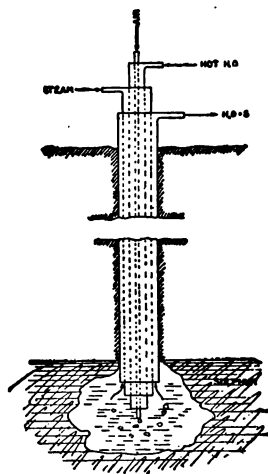
Fig. 83

391. Purification of sulphur. Sulphur is purified by distillation into large brick condensing chambers (Fig. 84). When the

receiving chamber is cold, the sulphur condenses at once to a fine powder known as **flowers of sulphur.** As soon as the chamber has become warm the sulphur vapor condenses to the liquid. This is cast in cylindrical moulds and forms what is known as **roll sulphur.**
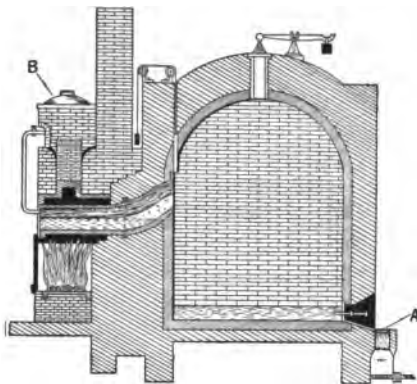
392. Production and use. The world produces about one million tons of sulphur a year, of which the United States produces about one-third. Sulphur is used primarily for the manufacture of sulphuric acid; also for

FIG. 84

the manufacture of sulphur dioxide, which is used in bleaching, in the manufacture of wood pulp, in the manufacture of gunpowder, matches, and rubber.

393. Common compounds. Sulphuric acid, H_2SO_4; hydrogen sulphide, H_2S; sulphur dioxide, SO_2; sodium sulphate, Na_2SO_4; calcium sulphate, $CaSO_4$; barium sulphate, $BaSO_4$; iron pyrites, FeS_2; galena, PbS.

Hydrogen Sulphide (Laboratory Exercise No. 19)

394. Appearance and occurrence. Hydrogen sulphide is a colorless, poisonous gas, with the odor of rotten eggs. It is found in the free condition in many natural springs, and it is always present during the decay of animal or vegetable matter containing sulphur.

395. Physical properties. The gas obeys Boyle's and Charles's laws and under the action of pressure and cold condenses to a colorless liquid.

If this liquid be allowed to evaporate rapidly, a portion of it is converted to a white solid. The liquid boils at $-62°$ and the solid melts at $-85°$.

Hydrogen sulphide is soluble in water, 1 volume of water

dissolving about 3 volumes of the gas. On boiling, all of the gas is expelled from the water. The molecular weight, determined from the gas density, is 34.3. The formula corresponding is H_2S.

396. Chemical properties. Hydrogen sulphide burns with a blue flame, giving the odor of sulphur dioxide. The products are water and sulphur dioxide. If the flame be caused to burn against a cold surface, a deposit of sulphur is formed:

$$2\ H_2S + O_2 = 2\ H_2O + 2\ S. \checkmark$$
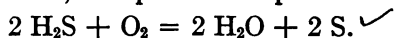
The water solution is a weak acid which changes blue litmus red and forms salts with bases. If this solution be allowed to stand, a deposit of sulphur is slowly formed; and if an oxidizing agent be added to it, the sulphur is instantly set free. This fact should constantly be borne in mind, for the student very frequently passes the gas into a solution that contains nitric acid and he is apt to mistake the resulting precipitate of sulphur for a sulphide:

$$2\ HNO_3 = H_2O + 2\ NO + 3\ O \checkmark$$
$$\underline{3\ O + 3\ H_2S = 3\ H_2O + 3\ S} \checkmark$$
$$2\ HNO_3 + 3\ H_2S = 4\ H_2O + 2\ NO + 3\ S. \checkmark$$
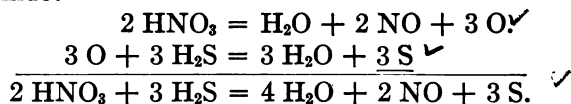
If the gas be passed in excess into a solution of sodium, potassium, or ammonium hydroxide, the acid salt is formed:

$$NaOH + H_2S = HNaS + H_2O.$$
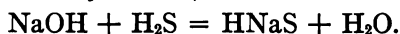
In order to convert this to the normal salt, an equal amount of the original solution of the alkali is added:

$$HNaS + NaOH = Na_2S + H_2O.$$
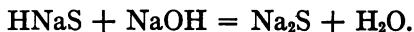
If the gas be passed into a solution of a salt that forms an insoluble sulphide, that sulphide is usually precipitated:

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$
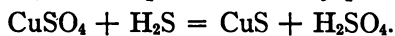
Some sulphides, however, while they are insoluble in neutral or alkaline solutions, are soluble in acids. In such cases the precipitation is incomplete, for the reason that there is enough acid formed by the reaction to reverse the action:

$$ZnSO_4 + H_2S \rightleftharpoons ZnS + H_2SO_4.$$

The gas itself, even in very dilute form, is very poisonous to animals and birds. Natural spring-waters containing it,

however, are much used as a beverage in the cure of certain diseases.

397. Test. A piece of filter-paper, moistened with a solution of a lead salt and ammonium hydroxide, is blackened when it comes in contact with the gas.

398. Preparation. It is commonly made by the action of a non-oxidizing acid on a sulphide. Dilute hydrochloric or sulphuric acid and ferrous sulphide are the reagents ordinarily used:

$$FeS + 2\ HCl = FeCl_2 + H_2S.$$
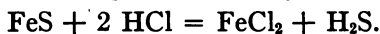
This is usually accomplished in a Kipp generator (Fig. 51), which serves very well for the preparation of small quantities of the gas. If larger quantities are needed to supply a large laboratory, it is convenient to make use of a large Parsons's generator (Fig. 85). This apparatus is made of acid-proof stoneware and consists of four parts: the reservoir jug, A, containing the acid inverted in a jar having a side outlet near the bottom; a cylindrical stone column, B, enlarged at the bottom, which stands in a jar, F. The upper portion of the column is filled with lumps of ferrous sulphide. As the acid runs down over the sulphide the gas accumulates in the space C until the pressure is great enough to stop the flow of the acid. The gas passes out through the wash-bottle, E, from which point it is distributed through pipes to the different outlets in the laboratory. The action is automatic, the gas being generated as fast as needed.
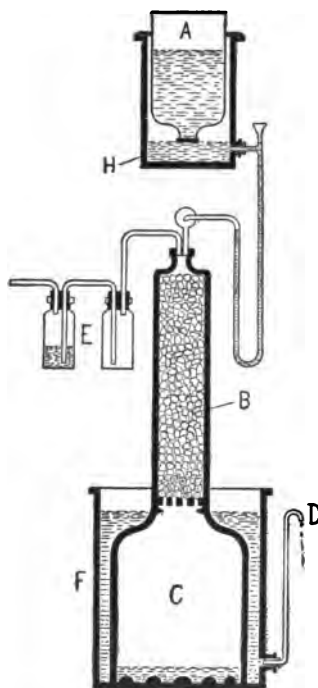
FIG. 85

399. Uses. The compound is much used in the laboratory for precipitating certain metals as sulphides, and also as a reducing agent. It is also used in the preparation and purification of many chemical compounds.

CHAPTER XXVIII

The Oxides and Oxygen Acids of Sulphur

Sulphur Dioxide (Laboratory Exercise No. 19)

400. Appearance and occurrence. Sulphur dioxide is a colorless gas with a suffocating odor of burning sulphur. It occurs free in the gases from active volcanoes and in river and spring waters that have their origin in volcanic regions.

401. Physical properties. The gas is readily condensed to a colorless liquid either by pressure or cold. If a stream of the gas be passed through a tube immersed in a freezing mixture of ice and salt, it is condensed to the liquid form. When exposed to the air, the liquid evaporates very rapidly, producing a low temperature. If about 10 c.c. of the liquid be quickly added to 5 c.c. of water contained in a red-hot platinum crucible where it remains quietly in the spheroidal form, the water is instantly frozen.

The critical temperature of the liquid is 156 and its critical pressure is 79 atmospheres (**164**).

One volume of water dissolves 50 volumes of the gas, forming a solution having the properties of a dibasic acid.

402. Chemical properties. The gas will not burn or support combustion, and it will not combine with oxygen when dry. Ordinary air mixed with sulphur dioxide passed over platinized asbestos at a temperature of 400° produces sulphur trioxide, the platinum acting as a catalytic agent, causing the oxygen to unite with the gas.

Colored flowers immersed in an atmosphere of moist sulphur dioxide are rapidly bleached.

The water solution of the gas is known as **sulphurous acid,** H_2SO_3. This solution has the properties of a weak dibasic acid.

When it is boiled all of the sulphur dioxide is given off, leaving nothing but water. In this respect it resembles a solution of carbon dioxide in water, which is known as carbonic acid. Sulphur dioxide and sulphurous acid both form stable salts with alkalies, known as sulphites:

$$SO_2 + 2\ NaOH = Na_2SO_3 + H_2O.$$
$$H_2SO_3 + 2\ NaOH = Na_2SO_3 + 2\ H_2O.$$
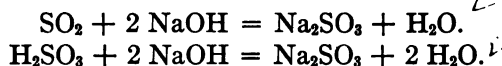
Sulphur dioxide and its solution are both powerful reducing agents, for the reason that, when mixed with a solution of an oxidizing agent, the sulphur is changed to its highest stage of oxidation, forming sulphuric acid or a sulphate.

Sulphurous acid instantly decolorizes a solution of potassium permanganate, according to the equations:

$$2\ KMnO_4 = K_2O + 2\ MnO + 5\ O.$$
$$5\ O + 5\ H_2SO_3 = 5\ H_2SO_4.$$
$$K_2O + H_2SO_4 = K_2SO_4 + H_2O.$$
$$2\ MnO + 2\ H_2SO_4 = 2\ MnSO_4 + 2\ H_2O.$$
$$\overline{2\ KMnO_4 + 5\ H_2SO_3 = 2\ H_2SO_4 + K_2SO_4 + 2\ MnSO_4 + 3\ H_2O.}$$
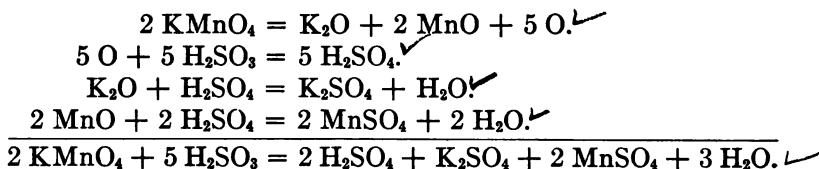
It also decolorizes bromine water for the same reason:

$$Br_2 + H_2O = 2\ HBr + O$$
$$O + H_2SO_3 = H_2SO_4.$$
$$\overline{Br_2 + H_2SO_3 + H_2O = H_2SO_4 + 2\ HBr.}$$
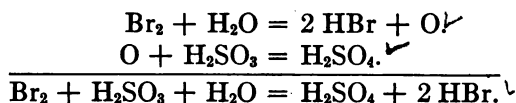
Nitric acid oxidizes sulphurous acid to sulphuric acid with the evolution of red fumes:

$$2\ HNO_3 = H_2O + 2\ NO + 3\ O.$$
$$3\ O + 3\ H_2SO_3 = 3\ H_2SO_4.$$
$$\overline{2\ HNO_3 + 3\ H_2SO_3 = 3\ H_2SO_4 + H_2O + 2\ NO.}$$
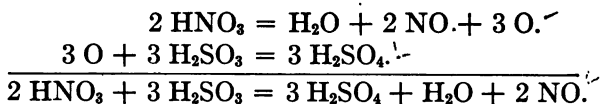
403. Test.   The free gas is usually recognized by its characteristic odor of burning sulphur.   If in solution, some barium chloride and a drop of hydrochloric acid are added.   No precipitate indicates the absence of a sulphate.   Almost any oxidizing agent, such as bromine water or concentrated nitric acid, may then be added.   If any sulphur dioxide or a sulphite is present, it will be changed to sulphuric acid or a sulphate and will give a white precipitate with the barium.

404. Preparation.

(1) It was first made in the laboratory by burning sulphur:

$$S + O_2 = SO_2.$$
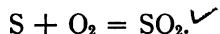
(2) It may also be made by treating a sulphite with an acid. This reaction is similar to the action of an acid on a carbonate.

The sulphurous acid which is formed is unstable and cannot exist in concentrated solution; it therefore breaks up into water and sulphur dioxide:

$$Na_2SO_3 + 2\,HCl = 2\,NaCl + H_2O + SO_2.$$
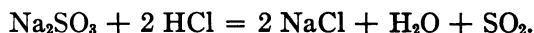
(3) By treating a thiosulphate with an acid:

$$Na_2S_2O_3 + 2\,HCl = 2\,NaCl + \underline{S} + H_2O + SO_2.$$

(4) It may be made by boiling concentrated sulphuric acid with certain metals and other substances that combine with oxygen. These substances, acting as reducing agents, extract one atom of oxygen from the acid, reducing it to sulphurous acid. This being unstable breaks up into sulphur dioxide and water.

$$H_2SO_4 = H_2O + SO_2 + O.$$
$$O + Cu = CuO.$$
$$\underline{CuO + H_2SO_4 = CuSO_4 + H_2O.}$$
$$2\,H_2SO_4 + Cu = CuSO_4 + 2\,H_2O + SO_2.$$
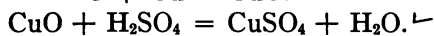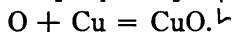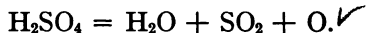
In a similar way, without writing the partial equations, we have:

$$2\,H_2SO_4 + C = 2\,H_2O + 2\,SO_2 + CO_2.$$
$$2\,H_2SO_4 + S = 2\,H_2O + 3\,SO_2.$$
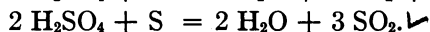
(5) It is produced on an enormous scale for the manufacture of sulphuric acid both by burning sulphur and certain sulphides, especially iron pyrites, FeS_2.

405. Uses. Sulphur dioxide is used for the manufacture of sulphuric acid, for the manufacture of acid calcium sulphite, which is used in the preparation of wood pulp, for the preparation of sulphites, and in the laboratory as a reducing agent.

406. Sulphur trioxide. This substance, as it ordinarily appears, is a feathery white solid which fumes in moist air. It has a great attraction for water with which it combines, with the liberation of a large amount of heat, to form sulphuric acid.

It may be made in the laboratory by passing a mixture of sulphur dioxide and air or oxygen through a tube filled with platinized asbestos which is maintained at a temperature of about 400°.   It is manufactured on a large scale in the "contact process" for the manufacture of sulphuric acid.

Sulphuric Acid (Laboratory Exercise No. 20)

407. Among all the artificial compounds known to man, sulphuric acid is the most important.   A larger quantity is annually manufactured than of any other chemical substance. This may be the more readily understood when it is realized that there is probably no finished artificial product in the course of whose manufacture sulphuric acid has not been used, either directly or indirectly.

408. Appearance.   When pure, sulphuric acid is a colorless, heavy, oily liquid.   If it is impure or has been exposed to dust, it often is dark-colored.   This color is due to finely divided particles of carbon resulting from the disintegration of organic material.

409. Physical properties.   The common concentrated acid of the laboratory has a specific gravity of 1.84 and contains about 98.3 per cent H_2SO_4.   It mixes with water in all proportions, forming dilute sulphuric acid.   When the acid and water are mixed there is always a rise in the temperature of the mixture. **The water should never be poured into the acid but always the acid into the water.**   This is because there is so much heat produced when the water is poured into the acid that some of the water is turned to steam and some of the acid mixture may be thrown out of the vessel.

Hot concentrated acid should not be poured into water for the same reason.

Sulphuric acid has a great tendency to absorb moisture.   If the acid be left exposed to the air it very rapidly increases in bulk for the reason that it attracts the moisture from the air.

The acid not only has a great affinity for water, but it will extract oxygen and hydrogen in the proportions to form water from substances containing them.   Most organic substances containing hydrogen and

oxygen are entirely disintegrated by the action of the acid, leaving a black mass of finely divided carbon. This is chiefly due to the extraction from them of oxygen and hydrogen in the proportion to form water. Sugar, cotton, paper, and wood are so blackened.

If the dilute acid be boiled the water evaporates with constantly rising temperature until the acid is concentrated; it then boils at a temperature of 330°. Some time before it boils it begins to give off dense white fumes. This is due to the partial dissociation of the acid into water and sulphur trioxide. If these fumes be passed through a condenser the water and anhydride reunite, forming the acid.

410. (1) **Chemical properties.** Dilute sulphuric acid is sour to the taste, turns litmus paper red, and neutralizes bases with the formation of water and salts. The solution contains the ions H, HSO_4, and SO_4, as well as much undissociated H_2SO_4.

(2) The acid is **dibasic**; that is, it contains 2 replaceable hydrogens; therefore, if it be treated with but 1 molecular weight of a mon-acid base such as sodium hydroxide, an acid salt is formed:

$$NaOH \leftrightarrows Na^+ + OH^-.$$
$$H_2SO_4 \leftrightarrows H^+ + HSO_4^-.$$
$$\overline{NaOH + H_2SO_4 = HOH + Na^+ + HSO_4^-.}$$
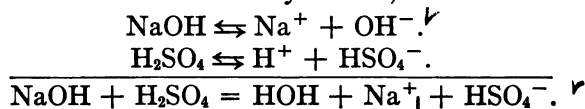
The formation of undissociated water accounts for most of the heat of the reaction. When the solution is evaporated, the Na ions and the HSO_4 ions unite to form the acid salt $HNaSO_4$, which is called **acid sodium sulphate,** or **hydrogen sodium sulphate.**

(3) When the dilute acid is mixed with a salt of a volatile and unstable acid, the latter is formed in too large a quantity to remain in solution and escapes with decomposition producing effervescence:

$$Na_2CO_3 \leftrightarrows Na^+ + Na^+ + CO_3^{--}.$$
$$H_2SO_4 \leftrightarrows H^+ + H^+ + SO_4^{--}.$$
$$\overline{Na_2CO_3 + H_2SO_4 = Na^+ + Na^+ + H_2CO_3 + SO_4^{--}.}$$
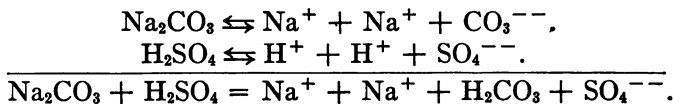
The compound H_2CO_3 is hydrogen carbonate or carbonic acid, an extremely unstable compound that cannot exist in strong solution.

It therefore breaks up into water and carbon dioxide, the gas escaping and producing an effervescence. The equation is usually written:

$$H_2SO_4 + Na_2CO_3 = Na_2SO_4 + H_2O + CO_2.$$

The **dilute acid** reacts with many metals, forming salts and hydrogen. It does not, however, sensibly attack platinum, gold, copper, or lead. It unites readily with basic oxides, forming water and salts, especially in the cases where the salts are soluble.

(4) **The cold concentrated** acid does not react readily with many of the metals that are easily attacked by the dilute acid.

If the concentrated acid be suddenly heated, it is broken up completely into water, sulphur dioxide, and oxygen; it is therefore distinctly an oxidizing agent. Boiling concentrated sulphuric acid will oxidize almost any substance that admits of being oxidized. This results, of course, in the production of sulphur dioxide. In the case of metals that form basic oxides, the oxide is at once converted to the corresponding sulphate by the excess of acid present:

$$H_2SO_4 = H_2O + SO_2 + O.$$
$$O + Cu = CuO.$$
$$CuO + H_2SO_4 = CuSO_4 + H_2O.$$
$$\overline{2\,H_2SO_4 + Cu = CuSO_4 + 2\,H_2O + SO_2.}$$
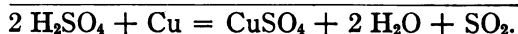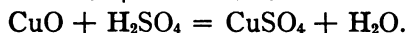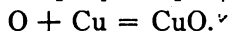
If a salt of a volatile and stable acid be treated with concentrated sulphuric acid, the other acid is always formed in sufficient quantity to produce a state of equilibrium:

$$Zn(NO_3)_2 + H_2SO_4 \leftrightarrows ZnSO_4 + 2\,HNO_3.$$
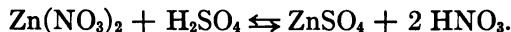
If this mixture be heated, the volatile acid escapes and more of the salt takes part in the reaction until all of the volatile acid has been driven off and the reaction is complete.

411. Test for the sulphate ion. Free sulphuric acid may usually be recognized by some of its characteristic properties.

In order to detect the presence of the sulphate ion, it is only necessary to add a solution of some substance containing a positive ion that forms a sulphate insoluble in dilute hydrochloric acid. Soluble salts of barium, strontium, or lead would serve the purpose. A solution of barium chloride is the reagent commonly used. If a few drops of this solution give a precipitate insoluble in dilute hydrochloric acid, the unknown solution contains a sulphate. Many solutions other than sulphates would also give white precipitates with barium, but these precipitates are all soluble in hydrochloric acid:

$$Na_2SO_4 + BaCl_2 = \underline{BaSO_4} + 2\,NaCl.$$
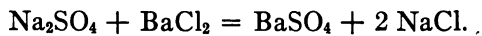
412. Preparation. (1) In the laboratory sulphuric acid is usually made as follows: Some sulphur is burned in a bottle containing water:

$$S + O_2 = SO_2.$$
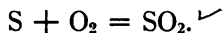
The bottle is then shaken to cause the SO_2 to dissolve in the water, forming a solution of sulphurous acid:

$$SO_2 + H_2O = H_2SO_3.$$
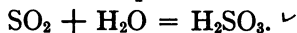
A suitable oxidizing agent is then added which oxidizes the sulphurous acid to sulphuric. Nitric acid, the red fumes of nitric acid, hydrogen peroxide, bromine or chlorine water would suffice. The acid is formed in very small quantities and is very dilute. It is best recognized by adding barium chloride:

$$2 HNO_3 = H_2O + 2 NO + 3 O.$$
$$3 O + 3 H_2SO_3 = 3 H_2SO_4.$$

(2) It might also be made by passing a mixture of sulphur dioxide and oxygen through a tube containing platinized asbestos. The finely divided platinum, acting as a catalytic agent, causes the oxygen to combine directly with the sulphur dioxide, forming sulphur trioxide. When this product is dissolved in water sulphuric acid is formed:

$$2 SO_2 + O_2 = 2 SO_3.$$
$$SO_3 + H_2O = H_2SO_4.$$
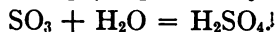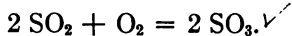
This process is known as the **contact process** and has lately come into very extensive use on a large scale.

(3) **Technical processes. The lead-chamber process.** In this process either sulphur or iron pyrites is burned, giving sulphur dioxide. This gas, together with steam, oxides of nitrogen, and air, is caused to pass into a large lead chamber or series of chambers, where the reactions take place and sulphuric acid collects at the bottom. The apparatus is so arranged that the oxides of nitrogen cannot escape and are used over and over again, acting as a catalytic agent between the oxygen of the air and the sulphurous acid.

The reactions are essentially as follows:

$$S + O_2 = SO_2.$$
$$SO_2 + H_2O = H_2SO_3.$$
$$N_2O_3 + H_2SO_3 = H_2SO_4 + 2 NO.$$
$$2 NO + air = N_2O_3.$$
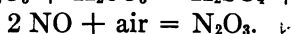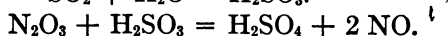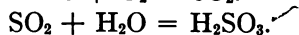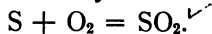
(4) **The lead-chamber process in greater detail.** Fig. 86 is strictly diagrammatic, and is sufficient to explain the process. *C* is a large lead chamber, which may be 40 ft. wide, 40 ft. high, and 100 ft. long. *A* is known as a **Glover** tower and is filled loosely with pieces of quartz stone or other acid-proof material. *B* is known as a **Gay Lussac** tower and is also filled loosely with acid-proof material. *D* is a furnace suit-
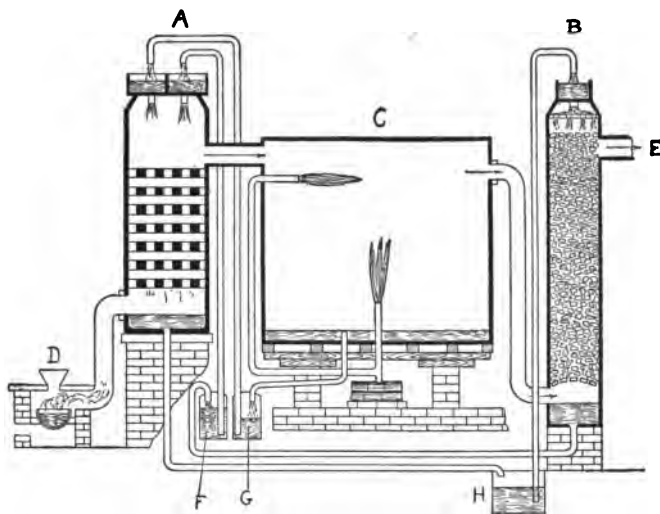
FIG. 86

able for burning sulphur or iron pyrites. *E* is a stack or suction device sufficient to produce a draught through the whole system. The hot gases from the furnace pass up through the Glover tower, heating the stones very hot. The reactions take place in the lead chamber, *C*, and dilute sulphuric acid settles out in the bottom of this chamber. This dilute acid is forced from the reservoir *G* up to the top of the Glover tower and is allowed to trickle down over the hot stones and comes out into the reservoir *H* very much concentrated. If some precautions were not taken, all of the oxides of nitrogen would escape into the air, and the process would be very expensive. To prevent this, all of the escaping gases are caused to pass up through the Gay Lussac tower, down which a stream of strong sulphuric acid is kept constantly flowing. The strong acid dissolves the oxides of nitrogen and forms what is known as nitrosyl sulphuric acid, which collects in the reservoir *F*. From this point the nitrosyl acid, is forced to the top of the Glover tower, where it mixes with the dilute sulphuric acid, which causes the liberation of the oxides of nitrogen. Thus the oxides of nitrogen are kept circulating about the lead chamber and cannot escape. There is a small loss, however, and from time to time more nitric acid is added to the top of the Glover tower.

(5) **Other methods.** Sulphuric acid is prepared as a by-product at many works where sulphur dioxide would otherwise be a waste product or would be a nuisance to the neighborhood if allowed to escape.

(6) It is also obtained in solution in the laboratory when hydrogen sulphide acting on a solution of a sulphate produces a precipitate of the metal as a sulphide:

$$H_2S + CuSO_4 = \underline{CuS} + H_2SO_4.$$
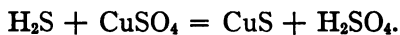
413. Uses. Sulphuric acid is used in larger quantities than any other strictly artificial chemical compound. It is necessary, either directly or indirectly, in the preparation of almost every finished product known to mankind.

Phosphate rock treated with the acid is rendered available for use in fertilizers. Hydrochloric, nitric, and other acids are prepared by the action of sulphuric acid on their salts.

It is used in the manufacture of sodium carbonate by the Le Blanc process, in the refining of petroleum, the preparation of hydrogen for balloons, of aniline dyes, and in the manufacture of all kinds of hardware.

CHAPTER XXIX

Nitrogen and Ammonia

Nitrogen (Laboratory Exercise No. 22)

414. Appearance and occurrence in the free condition. Nitrogen is a colorless gas without odor or taste. It occurs in the free condition in the atmosphere, forming about four-fifths of the air by volume.

415. Occurrence in the combined condition. Nitrogen occurs combined in the form of nitric acid and nitrates, in ammonia and ammonium compounds.

It is also an important constituent of nearly all vegetable and animal matter. Sodium nitrate, known as **Chili saltpetre,** is found in large deposits in Chili and Peru. Nitric acid and ammonia are both found in the atmosphere in small quantities.

416. Physical properties. At a constant pressure its volume varies as its absolute temperature (**Charles's law**); at a constant temperature its volume varies inversely as the pressure (**Boyle's law**).

When sufficiently cooled it condenses to a colorless liquid, and this, on further cooling, changes to a white solid. Solid nitrogen melts at $-210°$ and the liquid boils at $-196°$.

It is very slightly soluble in water, 1.7 volumes of the gas dissolving in 100 volumes of water at common temperatures.

417. Formula of nitrogen. Nitrogen is about fourteen times heavier than hydrogen and slightly lighter than air. 1 liter at normal temperature and pressure weighs 1.2507 g. One sixteenth of the weight of a liter of oxygen under the same conditions is .0893 g.

The density of nitrogen is the ratio of these two numbers, $\frac{1.2507}{.0893} = 14.$

Twice the gas density is the molecular weight, 28. Since the atomic weight is 14, there must be two atoms in the molecule and the formula for the element is N_2.

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418. Chemical properties. Unlike oxygen, nitrogen is very inactive and combines with almost nothing directly, under ordinary conditions. At high temperatures, however, it unites with many elements, forming nitrides. In many of these cases there is an absorption of heat instead of an evolution as in the case of oxygen.

Therefore, the chemical action will not proceed spontaneously when once started. In other words, if the nitrogen of the air started to combine with the oxygen, there would be no danger of the combination going very far, for there would be so much heat absorbed that there would not be enough left to enable the reaction to continue.

Chemical substances, the formation of which is accompanied by the absorption of heat, are known as **endothermic compounds.**

Nitrogen does not burn or support combustion. It unites directly with oxygen at high temperatures forming a series of oxides; and other oxides may easily be formed by indirect processes.

419. The oxides of nitrogen are as follows:

N_2O, nitrous oxide, or hyponitrous anhydride.

NO, nitric oxide.

N_2O_3, nitrogen trioxide, or nitrous anhydride.

NO_2, hot, or N_2O_4, cold, nitrogen dioxide or tetroxide.

N_2O_5, nitrogen pentoxide, or nitric anhydride.

The three anhydrides unite with water to form acids, as follows:

$$N_2O + H_2O = 2\ HNO,\ \text{hyponitrous acid.}$$
$$N_2O_3 + H_2O = 2\ HNO_2,\ \text{nitrous acid.}$$
$$N_2O_5 + H_2O = 2\ HNO_3,\ \text{nitric acid.}$$
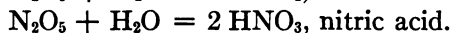
When an electric spark is passed through a mixture of nitrogen and hydrogen, the two gases combine to form nitrogen hydride, or ammonia gas, NH_3:

$$N_2 + 3\ H_2 \rightleftharpoons 2\ NH_3.$$
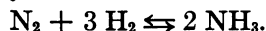
At high temperatures nitrogen combines directly with many metals, especially with magnesium, with which it forms **magnesium nitride, Mg_3N_2.**

420. Test. If the element is in the free condition, it may be recognized by the fact that it will not burn or support com-

bustion and has no odor. Still better, if it be mixed with oxygen and sparks from an induction-coil be passed through the mixture, red fumes will be formed.

421. Preparation. (1) The atmosphere consists of about four-fifths nitrogen and one-fifth oxygen. Nitrogen is commonly prepared in the laboratory by removing the oxygen from a portion of the air. It is evident that nitrogen prepared in this way must contain any other inert gas that the air happens to contain, and should therefore be called **atmospheric nitrogen,** to distinguish it from chemically pure nitrogen prepared in other ways.

If a piece of phosphorus on a cork floating on water be ignited and covered with a bell jar, the phosphorus will continue to burn until all of the oxygen in the jar has entered into combination with it (Fig. 87). During the burning the water gradually rises to take the place of the oxygen. The dense white clouds of smoke are chiefly phosphorus pentoxide, P_2O_5, mixed with some P_2O_3. On standing, these oxides dissolve completely in the water, forming phosphoric and phosphorous acids; and the atmospheric nitrogen is left perfectly clear. The water usually rises more than enough to fill the jar one-fifth full; for, when the jar was first put over the burning phosphorus, the air was expanded by the heat and some of it escaped. On cooling, an equal amount of water enters to take its place.
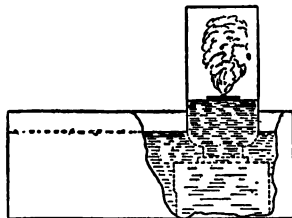
FIG. 87

This atmospheric nitrogen contains nearly 1 per cent of a very inert gas called **argon.**

(2) Atmospheric nitrogen could also be prepared by passing air through a red-hot tube filled with iron nails. The oxygen of the air would all combine with the iron, forming iron oxide, and atmospheric nitrogen would issue from the other end.

(3) Nitrogen may be prepared in a strictly chemical way by heating a solution of ammonium nitrite in a flask and collecting the gas over water (Fig. 88). As ammonium nitrite is

not to be had in the laboratory, a mixture of sodium nitrite
and ammonium chloride may be used instead:

$$NH_4Cl + NaNO_2 = NH_4NO_2 + NaCl.$$
$$NH_4NO_2 \text{ heated} = N_2 + 2 H_2O.$$
$$\overline{NH_4Cl + NaNO_2 = N_2 + 2 H_2O + NaCl.}$$
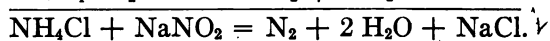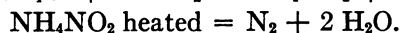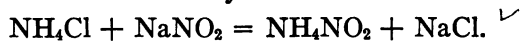
422. Uses. Nitrogen as an element is not used to any
great extent. It is of value, however, in cases where a perfectly
inert gas is necessary for
carrying out scientific ex-
periments; and it is some-
times used for filling the
capillary tubes above the
mercury in thermometers.

There are some recent
successful processes which
bring about the direct union
of the oxygen with the ni-
trogen of the atmosphere,
forming oxides of nitrogen.

FIG. 88

These oxides are then con-
verted to nitric acid, nitrates, and nitrites.
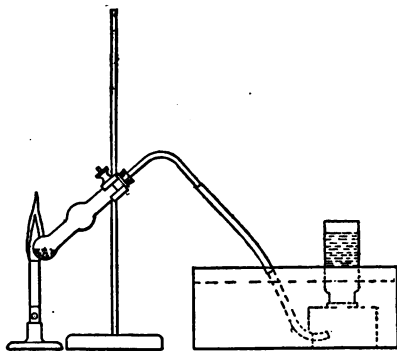
Nitrogen in the combined form is essential to plant life;
and, as the soil does not contain an unlimited supply, the nitro-
gen must be renewed from time to time by the addition of
fertilizers containing it. Fertilizer mixtures usually contain
phosphoric acid in the form of phosphates, potash in the form
of carbonate, chloride, or nitrate, and nitrogen in the form of
organic material of either animal or vegetable origin, ammonium
compounds, or nitrates.

423. Common compounds. Ammonia, NH_3; nitric acid, HNO_3;
nitrous oxide, N_2O; nitric oxide, NO; sodium nitrate, or Chili salt-
petre, $NaNO_3$; potassium nitrate, or saltpetre, KNO_3.

Ammonia (Laboratory Exercise No. 22)

424. Appearance and occurrence. Ammonia is a colorless gas
with a characteristic suffocating odor. It occurs free in the
air in minute quantities and is found in all natural spring

and river waters. It is also set free in all cases of organic decay.

425. Physical properties. Under ordinary conditions of temperature and pressure its volume varies directly as the absolute temperature and inversely as the pressure. When sufficiently compressed and cooled it condenses readily to the liquid form. Liquid ammonia boils at $-34°$ and freezes at $-76°$ to a white crystalline solid. The gas is extremely soluble in water. **One volume of water dissolves 1,148 volumes of the gas at 0°.** If this solution of ammonia in water be boiled or left exposed to the air, all of the gas escapes. The common household ammonia is nothing but a solution of the gas in water.

426. Chemical properties. Ammonia will not burn or support combustion under ordinary circumstances, but it will burn in an atmosphere of pure oxygen, forming water and nitrogen:

$$4\,NH_3 + 3\,O_2 = 6\,H_2O + 2\,N_2.$$
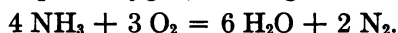
If sparks from an induction-coil be passed through ammonia gas, the latter is partially decomposed into nitrogen and hydrogen. This decomposition continues until a definite state of equilibrium is reached; that is, until the rate of recombination of the two gases is exactly equal to the rate of decomposition. This is another good example of a reversible reaction:

$$2\,NH_3 \leftrightarrows N_2 + 3\,H_2.$$
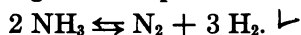
If a mixture of ammonia and oxygen be passed through a red-hot tube filled with copper oxide the gas will be entirely changed to nitrogen and water.

Ammonia combines very readily with all acids, forming what are known as **ammonium salts:**

$$NH_3 + HCl = NH_4Cl.$$
$$2\,NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$
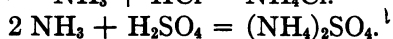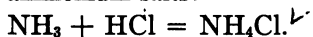
Ammonia gas dissolves in water with great readiness. Considerable heat is evolved during the process, which would indicate that it is not a case of mere mechanical solution. The resulting liquid is strongly alkaline and neutralizes acids just as other alkalies do. Assuming that a definite compound of ammonia and water is formed, the equation would be:

$$NH_3 + HOH \leftrightarrows NH_4OH.$$
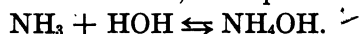
The proportions of ammonia and water called for by this equation are almost exactly the same as those in a saturated solution of the gas in water. The liquid is known as **ammonium hydroxide, ammonium hydrate, ammonia water, aqua ammonia,** or simply **ammonia.**

427. Test for ammonia. If the ammonia is in the free condition, it is readily recognized by its odor. It will also turn moist red litmus paper blue and will cause dense white fumes of ammonium chloride to form about the end of a glass rod moistened with hydrochloric acid.

If it is in the combined condition, as in an ammonium compound, it is first set free by means of a strong alkali, such as sodium hydroxide, and then recognized as free ammonia. In the case of a dry powder this is best done by grinding a small quantity in a mortar with sodium hydroxide solution and smelling for ammonia.

Fig. 89

428. Ammonia fountain. The extreme solubility of the gas in water may be well shown in the following manner: a long glass tube is drawn out at one end and passed through a rubber stopper with one hole, selected to fit a bottle, *A*. The bottle *A* is filled with dry ammonia gas, the stopper and tube are tightly inserted and the long end of the tube placed in a bottle, *B*, filled with water colored with red litmus solution. The colored water soon rises into the upper bottle and plays in the form of a fountain. The first water in the upper bottle absorbs all of the ammonia, forming ammonium hydroxide, which colors the red litmus water blue, and producing almost a vacuum. The atmospheric pressure acting on the surface of the water in the lower bottle continues to force the water into the upper. If the hole in the end of the tube is fine enough and the stopper in very tight, the fountain will continue to play for half an hour.

429. Preparation. When a dry ammonium salt is heated it breaks up into ammonia and the corresponding acid. As these two compounds reach a colder part of the apparatus, they recombine to form the original salt, so that ammonium compounds apparently sublime when heated. In order to obtain ammonia, then, it is only necessary to add some compound that will combine with the acid and prevent its escape. This is readily accomplished by adding a strong base or a basic oxide.

Sodium and potassium hydroxides and calcium oxide or hydroxide are commonly used. In the laboratory it is prepared by heating a mixture of 1 part of ammonium chloride and 2 parts of dry slaked lime (calcium hydroxide) in a flask (Fig. 90):

$$Ca(OH)_2 + 2\ NH_4Cl = CaCl_2 + 2\ H_2O + 2\ NH_3.$$

As the gas is lighter than air, it may best be collected in an inverted bottle. A drop of hydrochloric acid on the lip of the bottle shows when it is filled by giving off dense clouds of solid ammonium chloride.

Ammonia gas may also be readily obtained by heating some concentrated ammonia water in a flask.

430. Method of manufacture. Whenever any organic material containing nitrogen, such as animal or vegetable matter, or bituminous coal, is subjected to dry distillation, the nitrogen is converted to ammonia. In the manufacture of illuminating gas by the retort process bituminous coal is heated in retorts,

FIG. 90

and the gases are passed through water, which absorbs the ammonia and other impurities. This "ammonia liquor" is distilled with lime, and the ammonia that is set free is absorbed in sulphuric acid, forming crude ammonium sulphate; or else is purified at once and absorbed in water, or perhaps liquefied by pressure and cold and sold as anhydrous liquid ammonia.

Great quantities of ammonia or ammonium sulphate are obtained in a similar way from the gases produced in coke-ovens and blast-furnaces.

431. Other methods. If electric sparks be passed through a mixture of hydrogen and nitrogen, combination takes place, until a definite condition of equilibrium is established; that is, until the rate of formation is just equalled by the rate of decomposition:

$$N_2 + 3\ H_2 \leftrightarrows 2\ NH_3.$$
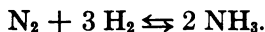
If an acid were present, the ammonia would be absorbed as fast as formed, and the reaction would go on to completion.
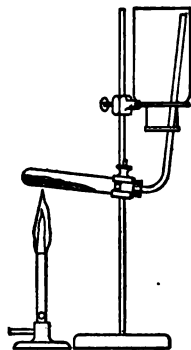
432. Uses. Ammonia is primarily used for the production of crude ammonium sulphate. A rough estimate of the quantity of this product produced yearly in the world would be 1,000,000 tons. This ammonium sulphate is largely used in the manufacture of artificial fertilizers, but it is also the starting-point in the manufacture of pure ammonia and all other ammonium compounds.

Anhydrous liquid ammonia is used in the manufacture of artificial ice.

A typical ammonia ice-plant consists of three essential parts (Fig. 91): a large tank, B, containing a strong solution of com-
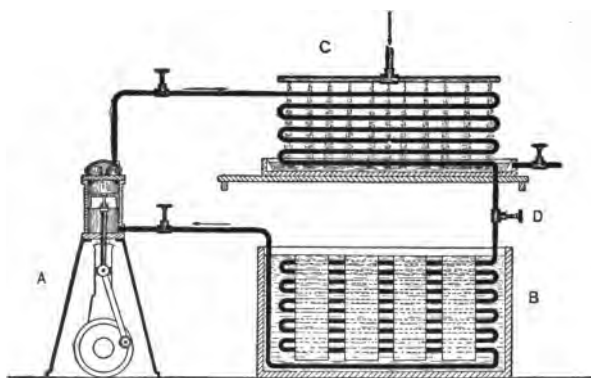
FIG. 91

mon salt or calcium chloride, immersed in which are a great many pipes containing liquid ammonia; an ammonia pump and compressor, A, which is constantly pumping ammonia gas out of the pipes in B; and a condenser, C, in which the same pump compresses the gas sufficiently to cause it to become liquefied with the help of cold water kept circulating through the condenser. The liquid ammonia returns to the tank through the reducing valve D.

The result of this continuous process is that the heat necessary to cause the liquid ammonia to evaporate is removed from the brine, and the temperature of the latter falls well below the freezing-point of fresh water. Galvanized-iron boxes of the shape of the block of ice desired, are filled with pure

water and immersed in the brine; and in the course of a day or two the water is frozen to a solid block of ice.

Ammonia is also a great cleansing agent and is sold throughout the land in the form of a dilute solution in water as "household ammonia."

433. Common compounds. Ammonium chloride, or sal ammoniac, NH_4Cl; ammonium sulphate, $(NH_4)_2SO_4$; ammonium nitrate, NH_4NO_3; and ammonia alum, $(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 + 24\ H_2O$.

CHAPTER XXX

THE ATMOSPHERE

(Laboratory Exercise No. 21)

434. Constituents. The atmosphere is essentially a mechanical mixture of oxygen and nitrogen in the proportion of about one-fifth oxygen and nearly four-fifths nitrogen. The mixture, however, contains several other gaseous elements which are present in fixed proportions, as well as some compounds that are present in variable proportions.

Constant Constituents	By volume
Nitrogen	78%
Oxygen	21%
Argon	00.94%
Helium	00.000001%
Neon	00.00001%
Krypton	00.000001%
Xenon	00.00000005%

Variable Constituents	
Water	1.4%
Carbon dioxide	00.03%
Ozone	
Hydrogen peroxide	
Ammonia	
Nitric acid	
Dust	
Microbes (bacteria)	

435. Air a mechanical mixture. The reasons for believing the air to be a mechanical mixture are as follows:

(1) If oxygen and nitrogen be mixed in the exact proportions in which they exist in the air, there is no evolution or absorption of heat and the resulting gas has all of the common properties of air.

(2) The composition of air is not always the same. If air that has been dissolved in water be examined, it is found that the oxygen and nitrogen have been dissolved in different proportions from those in which they exist in the air. This would be impossible, if the air were a chemical compound.

(3) The proportions by volume in which the two gases exist in the air

do not form a simple ratio, as they would have to if they were present as a compound. That is, the relative volumes of oxygen and nitrogen are nearly as 1 to 4, but not exactly.

436. Atmospheric nitrogen. If a quantity of air be passed through a red-hot tube filled with copper or iron turnings, all the oxygen will adhere to the metal, forming an oxide, and atmospheric nitrogen will be obtained. The weight of a liter of this gas is slightly greater than the weight of a liter of pure nitrogen prepared by the decomposition of some nitrogen compound. It ought to be perfectly evident, then, that atmospheric nitrogen is not pure, but must contain some other gas mixed with it.

437. Argon. Nearly 1 per cent of atmospheric nitrogen is argon, and it contains also very minute quantities of **helium, krypton, neon,** and **xenon.** A mixture of argon with these other gases may be obtained by causing atmospheric nitrogen to pass over magnesium at a high temperature. The nitrogen all combines with the magnesium, forming magnesium nitride, Mg_3N_2, and argon mixed with the other gases is left. Argon is a colorless gas that forms about .94 per cent of the atmosphere by volume. It may be liquefied and solidified. The solid melts at $-189°$, and the liquid boils at $-186°$. It is extremely inactive chemically and forms no known compounds. The gas is mon-atomic, the atomic and molecular weights being the same, 39.9. The symbol of the gas is A.

438. Helium. Helium was first discovered in the atmosphere of the sun by means of the spectroscope. It has also been shown by the same means that it exists in many fixed stars and nebulæ. In recent years it has been found in several minerals on the earth and in certain spring-waters. It also forms a very minute proportion of the atmosphere.

It may be obtained by the careful fractional evaporation or distillation of liquid atmospheric argon. It is very inactive and forms no known compounds with the elements. It has been liquefied and solidified. Its melting-point is $-271°$, and its boiling-point is $-267°$. It is monatomic, and its atomic weight is 4.

439. Neon, krypton, and **xenon.** These are very rare monatomic gases that exist in minute quantities in the atmosphere. They have been obtained by the careful fractional evaporation of liquefied atmospheric argon.

They form no known compounds with the elements. Their symbols and atomic weights are as follows:

Neon, Ne, 20; krypton, Kr, 81.8; xenon, Xe, 128.

The Variable Constituents of the Atmosphere

440. Carbon dioxide. The air normally contains .03 or .04 of 1 per cent of carbon dioxide by volume; that is, in 10,000 cu. ft. of air there would be 3 or 4 cu. ft. of the gas.

Carbon dioxide is being constantly given off by all forms of organic

decay; it is exhaled by animals of all kinds, and all fires are constantly producing quantities of the gas. One ton of hard coal when completely burned would produce about three tons of the gas or about 1,000,000 liters. It is perfectly plain, then, that there ought to be more than the normal amount of carbon dioxide in the atmosphere over large manufacturing cities.

The carbon dioxide of the air is constantly being absorbed by the leaves of growing plants. The carbon goes to form the woody fibre of the plant, and the oxygen is returned to the air.

441. Water vapor in the air. There is always water vapor in the air, but the amount is constantly changing with the temperature. When air at a given temperature is saturated with water it is said to be at the **dew-point.** The slightest reduction of the temperature will then cause a precipitation of some of the water in the form of fog or rain.

In summer the air frequently becomes saturated with moisture and further evaporation is almost prevented. The clothes will not dry quickly on such a day. The evaporation of the perspiration which ordinarily takes place without our knowledge and keeps us cool is prevented. The perspiration accumulates and we suffer from the heat and say it is a very "muggy" day. A change in the wind may cool the upper air below the dew-point and the excess of the moisture is precipitated as rain.

442. Ozone, hydrogen peroxide, ammonia, and nitric acid. Lightning discharges in the air cause the formation of small quantities of ozone and oxides of nitrogen. The water of the air acting on these forms hydrogen peroxide and nitrous and nitric acids. Ammonia is being constantly formed by the decay of organic matter containing nitrogen. The ammonia acting on the nitrous and nitric acids forms traces of the nitrite and nitrate. All of these things are washed out of the air by the rain and get into the soil, helping to fertilize it.

443. Dust. The dust is made up of small particles of every conceivable thing on the earth of both organic and inorganic nature. The dust particles include bacteria of all kinds, many of them being the germs of infectious diseases. The relative numbers of bacteria in two different localities may easily be compared by exposing two similar sterile gelatine plates for the same length of time at the two places. After the germs have grown enough to make spots on the plates the relative numbers may be counted.

444. Pressure of the atmosphere. The atmosphere presses down on the surface of the earth at the sea-level with a force of about 15 lbs. to the square inch. It is this pressure which causes the water to rise in the pipe of a suction-pump. The pump simply reduces the atmospheric pressure on the surface of the water inside of the pipe, and the atmospheric pressure on the surface of the water in the well literally pushes the water up the pipe. It is possible for such a pump at the sea-level to raise water 34 ft. Liquids heavier than water could not be raised as high.

If a glass tube more than 35 in. long be placed in a vertical position with the lower end in a vessel of mercury and the air pumped out from the upper end by means of a suitable air-pump, the mercury will rise until the weight of the column of mercury is exactly equal to the atmospheric pressure. This will be the case when the column is a little over 30 in. high. Any variation in the atmospheric pressure is at once shown by a change in the height of the mercury column. Such a column of mercury in a glass tube with a perfect vacuum above it is a mercurial barometer. Since the pressures are proportional to the heights of the columns, they are commonly spoken of in terms of either inches or millimeters.

Normal pressure is the average pressure at the sea-level and is taken as that equal to the weight of a column of mercury 760 mm. high.

445. Pressure of moist air. Avogadro's law states that equal volumes of all gases at the same temperature and pressure contain equal numbers of molecules. 1 liter of moist air, therefore, contains exactly the same number of molecules as 1 liter of dry air. The moist air does not weigh as much as the dry air for the reason that it is made up of molecules of oxygen, nitrogen, and water, with molecular weights of 32, 28, and 18, whereas the dry air contains nothing but oxygen and nitrogen molecules. When the atmosphere contains a large quantity of water vapor the pressure is not so great and the mercury column is correspondingly shorter.

446. The liquefaction of air. Any gas may be liquefied by subjecting it to both pressure and cold. In order to convert air to the liquid form it is first compressed to a pressure of about 3,000 lbs. to the square inch. The air before entering the compressor passes through several layers of cotton cloth, which remove the dust. On issuing from the compressor it passes successively through an oil separator, to remove oil carried over from the compressor; a cylinder containing potassium hydroxide, to remove the carbon dioxide; a cylinder containing calcium chloride, which removes the moisture; and a pre-cooler containing a freezing mixture of ice and alcohol, which not only removes the heat due to the compression but reduces the highly compressed air to a low temperature. The compressed air then enters the liquefier. This consists of a great length of very small copper tubing wound double in concentric layers about a

Fig. 92

vertical axis to form a cylinder. The whole is contained in a non-conducting casing. The compressed air is allowed to escape at the bottom
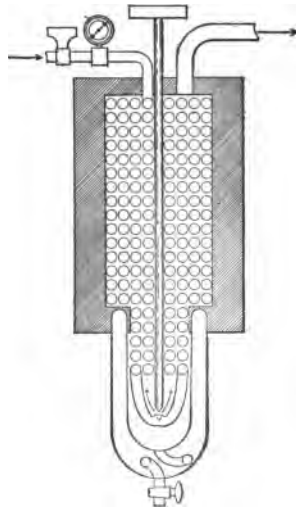
of one of the tubes, thereby producing a very low temperature. This cools the compressed air in the other tube sufficiently to liquefy it. The expanded air then goes back to the compressor (Fig. 92).
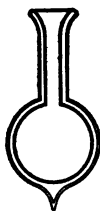
447. **Liquid air.** Liquid air is very light-blue in color and perfectly transparent. It is not strictly liquid air but a mixture of liquid oxygen and nitrogen, containing about equal quantities of each. Liquid nitrogen has a boiling-point of $-196°$ and liquid oxygen of $-184°$. Therefore, when the liquid mixture is allowed to evaporate slowly, the nitrogen escapes first, leaving almost pure liquid oxygen. Liquid air is kept in glass flasks with double walls, the air between which has been completely removed (Fig. 93).

FIG. 93

The inside surfaces of such flasks are very commonly covered with a coating of silver. It should be remembered that no liquid can evaporate without the aid of heat. The only way that heat can reach the liquid in such a flask is either by conduction through the walls or by the access of radiant heat from rays of light. The vacuum prevents any heat getting in by conduction, and the silvered surfaces reflect all light away.

The principle has recently been made use of in the manufacture of what are called "thermos bottles." These are very valuable for keeping liquids either hot or cold (Fig. 94).

FIG. 94

Liquid air is very commonly used for the production of low temperatures in scientific work.
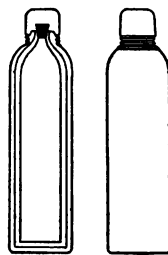
CHAPTER XXXI

THE OXIDES AND ACIDS OF NITROGEN

(Laboratory Exercise No. 23)

448. Nitrogen forms five different oxides as follows:

N_2O, nitrous oxide.

NO, nitric oxide.

N_2O_3, nitrogen trioxide, or nitrous anhydride.

NO_2, nitrogen dioxide, and N_2O_4, nitrogen tetroxide.

N_2O_5, nitrogen pentoxide, or nitric anhydride.

They are all endothermic, that is, they decompose with the evolution of heat and are therefore more or less unstable.

449. Nitrous oxide. Nitrous oxide is a colorless gas with a slightly sweet odor and taste, formed by heating ammonium nitrate (Fig. 95):

$$NH_4NO_3 = N_2O + 2 H_2O.$$

When heated this gas breaks up into nitrogen, and oxygen with the evolution of heat. For this reason, when ignited combustible substances are introduced into it, they burn almost as well as they would in pure oxygen.

It apparently supports the combustion of wood, paper, charcoal, sulphur, and phosphorus, nitrogen being set free:

$5 N_2O + 2 P = P_2O_5 + 5 N_2.$
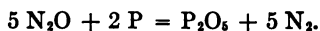
In order to distinguish it from oxygen, some nitric oxide, NO, might be mixed with it and there would be no change. With oxygen nitric oxide would produce a red gas.

FIG. 95

When inhaled, nitrous oxide produces temporary unconsciousness often accompanied by violent fits of laughing; hence it is sometimes called **"laughing gas."** It has been used
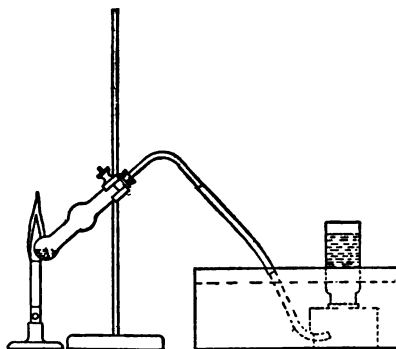
very generally by dentists to produce temporary unconsciousness in the patient during the extraction of teeth.

450. Nitric oxide. Nitric oxide is a colorless gas which is very commonly produced when dilute nitric acid and nitrates act as oxidizing agents. It is most easily prepared in the laboratory by allowing dilute nitric acid to act on copper, the evolved gas being collected over water. The apparatus may be arranged as in Fig. 96. About an ounce of scrap copper is placed in the bottle and the dilute acid (equal parts of acid and water) added through the funnel-tube.
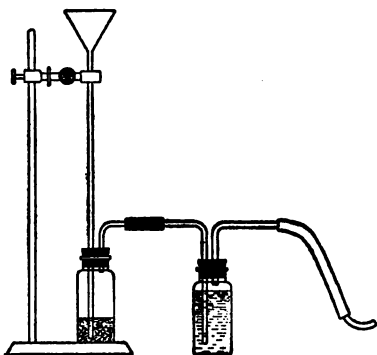
FIG. 96

Dilute nitric acid may be considered to oxidize as follows:

$$2 \text{ HNO}_3 = \text{H}_2\text{O} + 2 \text{ NO} + 3 \text{ O}.$$
$$3 \text{ O} + 3 \text{ Cu} = 3 \text{ CuO}.$$
$$3 \text{ CuO} + 6 \text{ HNO}_3 = 3 \text{ Cu(NO}_3)_2 + 3 \text{ H}_2\text{O}.$$
$$\overline{3 \text{ Cu} + 8 \text{ HNO}_3 = 3 \text{ Cu(NO}_3)_2 + 2 \text{ NO} + 4 \text{ H}_2\text{O}.}$$
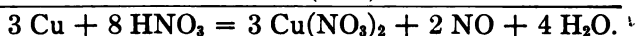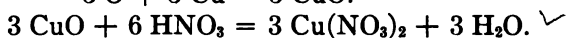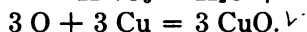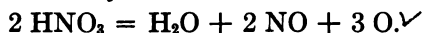
451. Properties. By far the most striking property of the gas is its tendency to combine with oxygen to form the red gas NO_2, nitrogen dioxide.

Very powerful reducing agents, such as sodium, potassium, or phosphorus, when intensely burning, will continue to burn when introduced into this gas; but ordinary burning substances, and even phosphorus when just ignited, are extinguished by it.

452. Nitrogen dioxide. Nitrogen dioxide is the red gas that is formed when colorless nitric oxide comes in contact with oxygen or air. It is a powerful oxidizing agent, and many substances that burn in air burn readily in it.

Its most striking property is its peculiar behavior when cooled or heated. When cooled sufficiently it becomes colorless on account of the formation of colorless nitrogen tetroxide:

$$2 \text{ NO}_2 \rightleftharpoons \text{N}_2\text{O}_4.$$
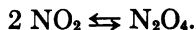
And when heated it again becomes colorless, because it is broken up into nitric oxide and oxygen:

$$2 \ NO_2 \leftrightarrows 2 \ NO + O_2.$$
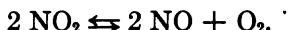
When dissolved in water it forms both nitric and nitrous acids:

$$2 \ NO_2 + H_2O = HNO_3 + HNO_2.$$

453. Nitrogen trioxide, N_2O_3. Nitrogen trioxide does not exist at the ordinary temperatures, on account of its tendency to break up into NO and NO_2.

A mixture of the two gases which will easily condense to a blue liquid may be obtained by boiling arsenic trioxide, or starch, with nitric acid, having a specific gravity of 1.3:

$$2 \ HNO_3 = H_2O + N_2O_3 + 2 \ O.$$
$$As_2O_3 + 2 \ O = As_2O_5.$$
$$\underline{As_2O_5 + 3 \ H_2O = 2 \ H_3AsO_4.}$$
$$2 \ HNO_3 + As_2O_3 + 2 \ H_2O = 2 \ H_3AsO_4 + N_2O_3.$$
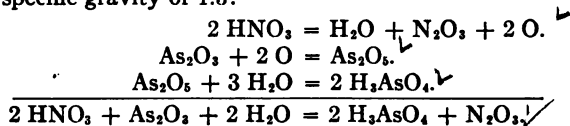
454. Nitrogen tetroxide, N_2O_4. Nitrogen tetroxide has already been referred to as a colorless gas formed by cooling the red gas NO_2. During the cooling each 2 molecules of the red NO_2 unite to form 1 molecule of the colorless gas N_2O_4. This compound may be considered as a mixed anhydride of nitric and nitrous acids; for, when it is mixed with water in the form of ice, both nitric and nitrous acids are formed:

$$N_2O_4 + H_2O = HNO_3 + HNO_2.$$

455. Nitrogen pentoxide, N_2O_5. Nitrogen pentoxide is an unstable, colorless, crystalline solid which breaks up into red oxides of nitrogen and oxygen.

It is the anhydride of nitric acid uniting with water with the liberation of much heat to form the latter:

$$N_2O_5 + H_2O = 2 \ HNO_3.$$
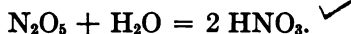
It may be prepared by distilling fuming nitric acid with phosphorus pentoxide:

$$2 \ HNO_3 + P_2O_5 = 2 \ HPO_3 + N_2O_5.$$
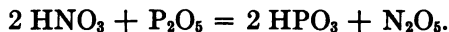
456. Nitrous acid, HNO_2. Nitrous acid exists only in dilute solution at low temperatures. The salts of nitrous acid are known as **nitrites,** and are stable.

If an acid be added to a strong solution of a nitrite, a copious evolution

of red oxides of nitrogen takes place. While the gas set free is theoretically the anhydride N_2O_3, on account of the dissociation of the latter, it is a mixture of the oxides NO and NO_2, the NO, of course, changing to NO_2 in the air. If the solution was cold, much of the N_2O_3 dissolves, producing a light-blue color.

Nitrites are nearly all derived from sodium nitrite, which is made by reducing melted sodium nitrate with lead:

$$KNO_3 + Pb = KNO_2 + PbO.$$
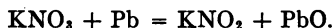
Nitric Acid, HNO_3

457. Appearance. Pure nitric acid is a colorless liquid which, when exposed to light or heat, is partly decomposed into water and red oxides of nitrogen and oxygen. Some of the red oxides remaining in solution color the acid yellow or red.

The common concentrated acid of the laboratory contains about 30 per cent water, and even this is often colored yellow or red by the action of direct sunlight.

458. Physical properties. The pure, or absolute, nitric acid mentioned above has a specific gravity of 1.56 and freezes to a white crystalline solid at $-47°$. It boils at $86°$, but the boiling is accompanied by partial decomposition into water, red oxides of nitrogen, and oxygen. This results in a gradual weakening of the acid due to the accumulation of water; and the boiling-point rises until it reaches $121°$, when equilibrium is established and there is no further change in the concentration.

Nitric acid, having a boiling-point of 120.5, a specific gravity of 1.40, and containing about 68 per cent acid, constitutes the ordinary concentrated reagent of the laboratory.

459. Chemical properties. Nitric acid is primarily an oxidizing agent. The degree of oxidation that takes place varies with the concentration of the acid, the substance acted upon, and the temperature.

It is made up of water combined with nitrogen pentoxide. Nitrogen pentoxide is nitrogen in its highest stage of oxidation. During oxidation the nitrogen drops to some lower stage and may even go down as far as ammonia, NH_3. The various ways in which the oxidation may take place are indicated by the following equations:

$$2 \, HNO_3 = H_2O + N_2O_5.$$
$$= H_2O + 2 \, NO_2 + O.$$
$$= H_2O + N_2O_3 + 2 \, O.$$
$$= H_2O + 2 \, NO + 3 \, O.$$
$$= H_2O + N_2O + 4 \, O.$$
$$= H_2O + N_2 + 5 \, O.$$
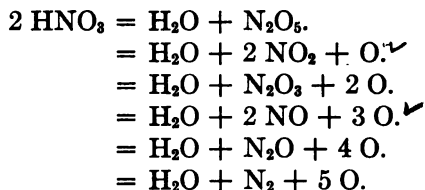
Nitric acid acts violently on most metals, with the formation of some of the reduction products, usually appearing in the form of red oxides of nitrogen.

In representing such reactions by equations it is best to assume that the metal is first oxidized to a basic oxide and then that this oxide dissolves in some more of the acid that is present. It is only necessary to know what the chief reduction product is. If the acid is very concentrated, much NO_2 will be formed and the equation could be worked out as follows:

$$2 \, HNO_3 = H_2O + 2 \, NO_2 + O.$$
$$O + Cu = CuO.$$
$$\underline{CuO + 2 \, HNO_3 = Cu(NO_3)_2 + H_2O.}$$
$$4 \, HNO_3 + Cu = Cu(NO_3)_2 + 2 \, NO_2 + 2 \, H_2O.$$
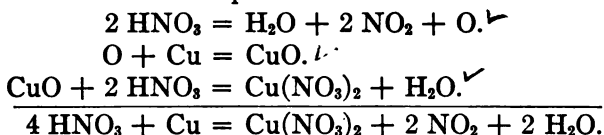
If the acid were more dilute, consisting of the ordinary concentrated acid of the laboratory with an equal volume of water, there would be much NO formed. In this case the equation could be worked out as follows:

$$2 \, HNO_3 = H_2O + 2 \, NO + 3 \, O.$$
$$3 \, O + 3 \, Cu = 3 \, CuO.$$
$$\underline{3 \, CuO + 6 \, HNO_3 = 3 \, Cu(NO_3)_2 + 3 \, H_2O.}$$
$$3 \, Cu + 8 \, HNO_3 = 3 \, Cu(NO_3)_2 + 4 \, H_2O + 2 \, NO.$$
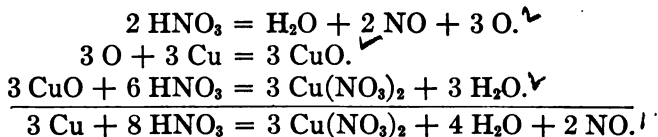
In the cases where nitric oxide, NO, is formed, when it comes in contact with the oxygen of the air it is immediately converted to NO_2, which is red.

With very dilute nitric acid zinc does not give any red fumes and some of the nitric acid is reduced to ammonia. In working out the equation for this reaction it may be assumed that nascent hydrogen is formed:

$$4 \, Zn + 8 \, HNO_3 = 4 \, Zn(NO_3)_2 + 8 \, H.$$
$$HNO_3 + 8 \, H = NH_3 + 3 \, H_2O.$$
$$\underline{NH_3 + HNO_3 = NH_4NO_3.}$$
$$4 \, Zn + 10 \, HNO_3 = 4 \, Zn(NO_3)_2 + NH_4(NO_3) + 3 \, H_2O.$$
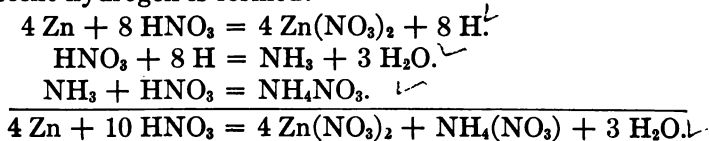
From what has been said about the various ways in which nitric acid may oxidize under different conditions, it is evident that the pupil often will not know what the chief reduction product is and therefore what amount of oxygen should be used.   In uncertain cases it may be well to assume invariably that 2 molecules of the acid give 2 molecules of nitric oxide, NO, and 3 atoms of oxygen for oxidizing purposes.

If the acid is perfectly free from oxides of nitrogen, its action on metals is very slow at first.   On heating, some oxides are formed by the partial decomposition of the acid, and the reaction proceeds with great violence accompanied by a copious evolution of red fumes.   This is evidently a case where the oxides act as catalytic agents.

Besides reacting with most metals to form the corresponding nitrates, with the evolution of oxides of nitrogen, nitric acid reacts with basic oxides and bases, forming nitrates and water.

The acid produces yellow spots on the skin and nails which will disappear only with the lapse of time.

460. Test.   For the free acid when present in considerable quantity, the best test is to add some copper to a small portion in a test-tube and heat it.   The instant evolution of red fumes is sure evidence of the nature of the liquid.

Fig. 97

For a small quantity of the acid, or the presence of a nitrate, proceed as follows: mix the solution to be tested with three times its bulk of concentrated sulphuric acid in a test-tube; add to this carefully, so as not to mix with it, a saturated solution of ferrous sulphate. If there is any nitric acid or nitrate present, there will be a brown ring in the zone between the two liquids.
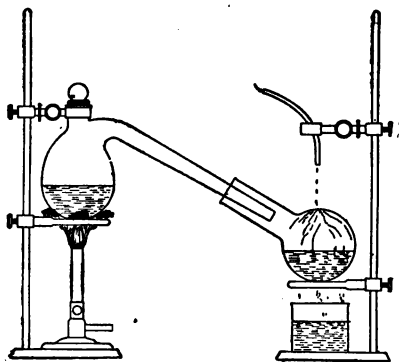
461. Preparation.   In the laboratory nitric acid is made by the action of sulphuric acid on either sodium or potassium nitrate.   The two substances, with a little water, are put in a

glass retort or suitable distilling bulb and connected with some kind of a condenser (Fig. 97). On heating, the nitric acid distils over into the receiver. Heating always decomposes some of the acid, and the distillate is colored yellow or red on account of the absorption of some of the red oxides of nitrogen. This color may be entirely removed by causing air to bubble through the liquid.

When sodium and potassium compounds are treated with sulphuric acid in excess in the laboratory the acid salts are always formed:

$$KNO_3 + H_2SO_4 = HKSO_4 + HNO_3.$$
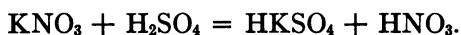
If no heat were applied, all four indicated compounds would exist in equilibrium in the mixture. Nitric acid, being more volatile than sulphuric, boils away when heat is applied, and the reaction goes on to completion.

462. Manufacture. The acid is manufactured on a large scale in essentially the same way that it is made in the laboratory,
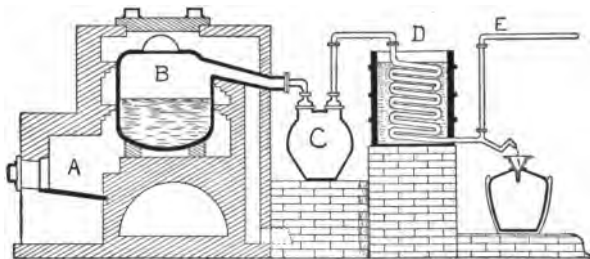
FIG. 98

except that the temperature is carried higher and a smaller quantity of sulphuric acid is used. This results in the formation of normal sodium sulphate.

Sodium nitrate, or "Chili saltpetre," is mixed with the proper quantity of sulphuric acid to form the normal sulphate in a large iron retort (Fig. 98). The nitric acid is condensed in earthenware vessels.

The reaction takes place in two stages:

$$NaNO_3 + H_2SO_4 = HNaSO_4 + HNO_3.$$
$$NaNO_3 + HNaSO_4 = Na_2SO_4 + HNO_3.$$
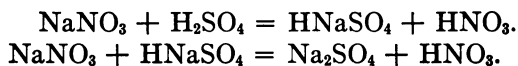
463. The Birkland and Eyde process. It has long been known that when an electric spark passes through a mixture of oxygen and nitrogen some oxides of nitrogen are formed.

Birkland and Eyde of Norway were the first to devise a practical process for making nitric acid and nitrates based on the above fact. They cause a current of air to pass through a chamber in which there is a large electric arc. The peculiarity of their process is that the arc is formed in a powerful magnetic field. This results in the arc spreading out in the form of a circular disk about 6 ft. in diameter. The air after passing through the chamber contains a very appreciable quantity of oxides of nitrogen. This air is passed through an absorbing tower, where it comes in contact with water. All of the NO_2 is absorbed, forming nitric and nitrous acids. On concentrating, some NO is given off, which is mixed with more air, forming NO_2, and sent through the absorbing tower again.

464. Other methods. Nitrogen pentoxide could be dissolved in water:

$$N_2O_5 + H_2O = 2\ HNO_3.$$

Nitric acid is frequently formed in reactions giving precipitates:

$$HCl + AgNO_3 = \underline{AgCl} + HNO_3.$$
$$Ba(NO_3)_2 + H_2SO_4 = \underline{BaSO_4} + 2\ HNO_3.$$
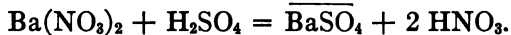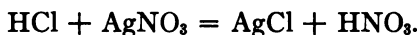
465. Uses. 1. It is used in the formation of nitrates, by its action on metals, basic oxides, bases, and carbonates.

2. For brightening brass and copper goods previous to lacquering.

3. For nitrating cotton and other substances, producing products much used in the manufacture of smokeless powder and high explosives.

4. For the manufacture of aniline dyes.

CHAPTER XXXII

Phosphorus, Arsenic, Antimony, and Bismuth

Phosphorus (Laboratory Exercise No. 25)

466. Appearance. There are two distinct varieties of phosphorus, commonly known as yellow crystalline and red amorphous. The common variety, when freshly prepared and perfectly pure, is a colorless, hornlike solid which soon turns yellow when exposed to light and becomes opaque. The amorphous phosphorus is a dark-red powder.

467. Occurrence. It is not found in the free condition, but occurs very widely distributed as calcium phosphate, $Ca_3(PO_4)_2$, also known as rock phosphate, especially abundant in Florida, Alabama, and North Carolina.

Bones contain a large percentage of calcium phosphate and, if the animal matter be removed by burning, the residue is almost pure calcium phosphate.

468. Physical properties. The yellow crystalline variety can be easily cut with a knife; it melts at 44°, boils at 287°, and has a specific gravity of 1.83 at 10°. It is readily soluble in carbon disulphide and insoluble in water. It is extremely poisonous. The molecule of phosphorus at ordinary temperatures contains 4 atoms, P_4. Above 1700° it is partly dissociated into molecules containing only 2 atoms, P_2.

The red amorphous variety is insoluble in carbon disulphide, is not poisonous, and is converted to the yellow variety by heat.

469. Chemical properties. Phosphorus is extremely active. It unites with the halogens with great violence and combines directly with oxygen. Yellow phosphorus bursts into flame when the temperature reaches 40°. The slow oxidation of the yellow variety is accompanied by a glow both of the element itself and the vapors coming from it, visible in the dark.

Hence any substance which glows in the dark is said to be phosphorescent.

The burning of phosphorus in oxygen or air is accompanied by an intense white light accompanied by a voluminous evolution of white smoke. This white smoke is chiefly phosphorus pentoxide, but it contains some phosphorus trioxide:

$$4 P + 5 O_2 = 2 P_2O_5.$$
$$4 P + 3 O_2 = 2 P_2O_3.$$
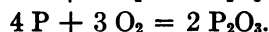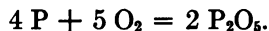
A solution of yellow phosphorus in carbon dioxide, when poured on filter-paper, soon causes the latter to burst into flame. This is because the solvent quickly evaporates and leaves a large surface of perfectly clean phosphorus exposed to the air. Oxidation starts at once, and the temperature soon rises to the igniting-point.

470. The oxides, P_2O_5 and P_2O_3, are both acidic and are the anhydrides of phosphoric and phosphorous acids. P_2O_5 unites with three different quantities of water, forming three different phosphoric acids as follows:

$$P_2O_5 + H_2O = 2 HPO_3, \text{ meta-phosphoric acid.}$$
$$P_2O_5 + 2 H_2O = H_4P_2O_7, \text{ pyro-phosphoric acid.}$$
$$P_2O_5 + 3 H_2O = 2 H_3PO_4, \text{ ortho-phosphoric acid.}$$
$$P_2O_3 + 3 H_2O = 2 H_3PO_3, \text{ ortho-phosphorous acid.}$$
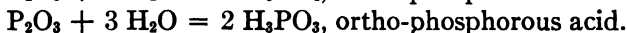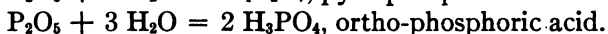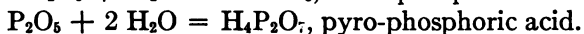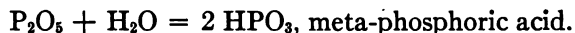
The gas density of gaseous phosphorus trioxide indicates the formula P_4O_6. It does, however, dissolve slowly in water and form some phosphorous acid. Although the formula of the acid shows 3 hydrogen atoms, only 2 of them can be replaced by metals.

Phosphorus forms several compounds with hydrogen, the commonest of which is **phosphine,** PH_3. This gas, as commonly prepared, is spontaneously inflammable in the air, and is best prepared by the action of calcium phosphide on water:

$$Ca_3P_2 + 6 H_2O = 3 Ca(OH)_2 + 2 PH_3.$$
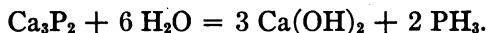
471. Action of oxidizing agents. On account of its tendency to combine with oxygen, phosphorus is a powerful reducing agent. Treated with an excess of almost any oxidizing agent in the presence of water, it is converted to phosphoric acid:

$$5 Br_2 + 5 H_2O = 10 HBr + 5 O.$$
$$2 P + 5 O = P_2O_5.\checkmark$$
$$\frac{P_2O_5 + 3 H_2O = 2 H_3PO_4.\checkmark}{5 Br_2 + 2 P + 8 H_2O = 2 H_3PO_4 + 10 HBr.}\checkmark$$
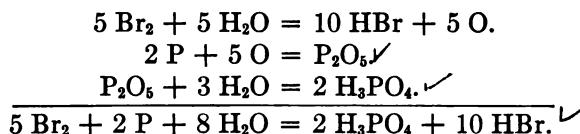
Note here that hydrobromic acid is made by making use of bromine as an oxidizing agent.

Nitric acid also converts phosphorus to phosphoric acid.

Since 2 molecules of nitric acid will furnish 3 atoms of oxygen and since 2 atoms of phosphorus require 5 atoms, it will be necessary to use 15 atoms:

$$10 HNO_3 = 5 H_2O + 15 O + 10 NO.$$
$$6 P + 15 O = 3 P_2O_5.\checkmark$$
$$\frac{3 P_2O_5 + 9 H_2O = 6 H_3PO_4.\checkmark}{10 HNO_3 + 6 P + 4 H_2O = 6 H_3PO_4 + 10 NO.}\checkmark$$
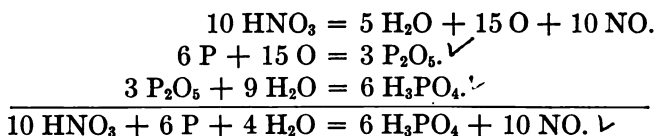
472. Test. Free phosphorus is recognized at once by its odor and phosphorescence. A phosphate with ammonium chloride, ammonium hydroxide, and a solution of a magnesium salt gives a white crystalline precipitate of ammonium magnesium phosphate:

$$Na_2HPO_4 + MgCl_2 + NH_4OH = \frac{NH_4MgPO_4 + 2 NaCl +}{HOH.}\checkmark$$
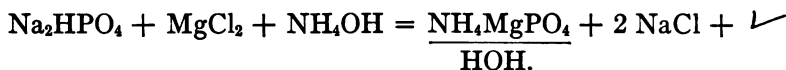
473. Preparation. Phosphorus is manufactured by heating a mixture of calcium phosphate, sand, and carbon to a very high temperature. The phosphorus is given off in the gaseous form and is condensed under water. This reaction is best carried out in an electric furnace (Fig. 99), which readily gives the high temperature required.

The calcium silicate runs off from time to time as a molten slag. The phosphorus is melted under water and cast into cylindrical sticks, which are afterward sealed in tin containers filled with water.

The steps in the reaction might be given as follows:

FIG. 99

$$Ca_3(PO_4)_2 + 3 SiO_2 = 3 CaSiO_3 + P_2O_5.$$
$$\frac{P_2O_5 + 5 C = 2 P + 5 CO.}{Ca_3(PO_4)_2 + 3 SiO_2 + 5 C = 2 P + 3 CaSiO_3 + 5 CO.}$$
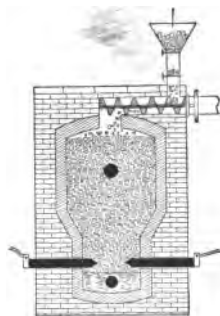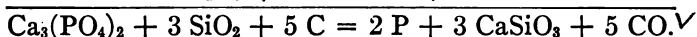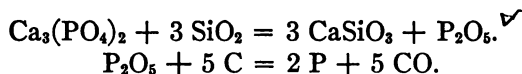
474. Uses. Phosphorus is chiefly used in the manufacture of matches. A match-head mixture consists of an oxidizing agent, such as manganese dioxide, red lead, or potassium chlorate; with a reducing agent, such as sulphur or antimony trisulphide; together with pulverized sand or glass and a little phosphorus. The whole mixture is made up with a solution of glue. Match-sticks tipped with this will ignite on any surface. The friction heats the phosphorus up to the ignition temperature. In the case of **safety matches,** which ignite only on the box, the phosphorus and some of the sand and antimony trisulphide are put on the box.

475. Compounds of phosphorus. Phosphorus pentoxide, P_2O_5, or phosphoric anhydride; phosphorus trioxide, P_4O_6, or phosphorous anhydride; phosphine, PH_3; **ortho-phosphoric acid, H_3PO_4; pyro-phosphoric acid, $H_4P_2O_7$; meta-phosphoric acid, HPO_3;** phosphorous acid, H_3PO_3; **hydrogen disodium phosphate, $HNa_2PO_4 \cdot 12\ H_2O$,** or common sodium phosphate; **microcosmic salt, $HNaNH_4PO_4 \cdot 4\ H_2O$; normal calcium phosphate, $Ca_3(PO_4)_2$,** rock phosphate, bone-phosphate, or bone-ash.

476. Phosphates in fertilizers. There are three important constituents of fertile soil which must be added in the form of fertilizers from time to time. They are **nitrogen** in some form—ammonium salts, nitrates, or organic matter containing nitrogen; **potassium** in some form—usually potassium carbonate, chloride, or sulphate; and **phosphorus,** usually in the form of phosphates. Rock phosphate and bone-dust are almost absolutely insoluble in water, and therefore are very slowly absorbed by the plant life. It is customary to treat the insoluble calcium phosphate with a certain quantity of sulphuric acid, in order to form the acid salt, which is soluble and therefore immediately available. The following equation indicates the reaction:

$$Ca_3(PO_4)_2 + 2\ H_2SO_4 = 2\ CaSO_4 + CaH_4(PO_4)_2.$$
$$310 \qquad\qquad 196$$
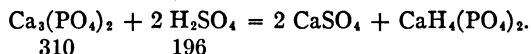
That is, to 310 weights of ground rock phosphate or ground bone 196 weights of sulphuric acid are added and thoroughly mixed. No attempt is made to separate the calcium sulphate, and the mixture is known as **acid phosphate.**

Arsenic (Laboratory Exercise No. 25)

477. Appearance and occurrence. Arsenic exists in two forms, a gray, crystalline, metallic substance and a black, amorphous solid. It occurs in both the free and combined conditions. The commonest natural compounds are the double sulphide of arsenic and iron known as **mispickel,** FeAsS; the sulphides known as **realgar,** As_2S_3; and **orpiment,** As_2S_3.

478. Physical properties. When arsenic is heated out of contact with air it sublimes readily, and condenses in the colder part of the apparatus into two distinct varieties. That portion nearest the heat resembles a gray, crystalline metal and the other a black, amorphous solid. The gray variety has a specific gravity of 5.73, and the black has a specific gravity of 4.71. The vapor density of the element at 644° indicates that the molecule contains 4 atoms, As_4. At a much higher temperature it splits into two diatomic molecules.

479. Chemical properties. Arsenic burns readily, with the formation of white clouds of arsenic trioxide, giving off an odor of garlic.

Although this white oxide is called **arsenic trioxide,** its vapor density indicates the formula As_4O_6. It dissolves to a very slight extent in water, forming arsenious acid:

$$As_4O_6 + 6 H_2O = 4 H_3AsO_3.$$
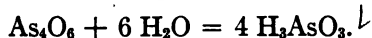
Arsenic also forms the oxide As_2O_5, but it cannot be prepared directly by burning the element. Arsenic acid is first prepared and then heated sufficiently to drive off the water:

$$2 H_3AsO_4 = As_2O_5 + 3 H_2O.$$

It is evident from the above that arsenic pentoxide is also acidic and is the anhydride of ortho-arsenic acid.

Arsenic forms arsenic acids exactly analogous to the phosphoric acids:

$$As_2O_5 + 3 H_2O = 2 H_3AsO_4, \text{ ortho-arsenic acid.}$$
$$As_2O_5 + 2 H_2O = H_4As_2O_7, \text{ pyro-arsenic acid.}$$
$$As_2O_5 + H_2O = 2 HAsO_3, \text{ meta-arsenic acid.}$$
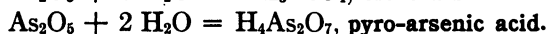
The element unites with most of the elements, forming binary

compounds. When boiled with oxidizing agents it is converted to arsenic acid:

$$5 I_2 + 5 H_2O = 10 HI + 5 O.$$
$$2 As + 5 O = As_2O_5.$$
$$As_2O_5 + 3 H_2O = 2 H_3AsO_4.$$
$$\overline{5 I_2 + 8 H_2O + 2 As = 2 H_3AsO_4 + 10 HI.}$$
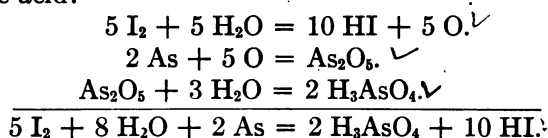
Arsenic trioxide dissolves in alkalies readily, forming arsenites:

$$As_4O_6 + 12 NH_4OH = 4 (NH_4)_3AsO_3 + 6 H_2O.$$
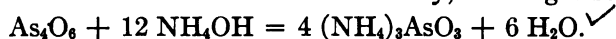
It also dissolves in hydrochloric acid, forming **arsenic trichloride**:

$$As_4O_6 + 12 HCl = 4 AsCl_3 + 6 H_2O.$$
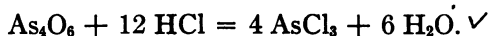
If hydrogen sulphide be passed into a solution of arsenic in either alkalies or acids, a yellow precipitate of **arsenic trisulphide** is obtained:

$$2 (NH_4)_3AsO_3 + 3 H_2S = 6 NH_4(OH) + As_2S_3.$$
$$2 AsCl_3 + 3 H_2S = As_2S_3 + 6 HCl.$$
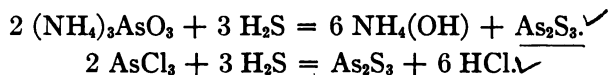
Arsenic trisulphide dissolves in alkali sulphides, forming soluble **thioarsenites**:

$$3 (NH_4)_2S + As_2S_3 = 2 (NH_4)_3AsS_3.$$
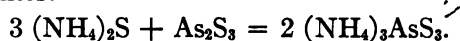
If this solution be treated with hydrochloric acid, arsenic trisulphide is reprecipitated, and ammonium chloride and hydrogen sulphide are formed:

$$2 (NH_4)_3AsS_3 + 6 HCl = As_2S_3 + 3 H_2S + 6 NH_4Cl.$$

Arsenic trisulphide dissolves in yellow ammonium sulphide (ammonium sulphide containing some dissolved sulphur), forming **ammonium thioarsenate**, $(NH_4)_3AsS_4$:

$$3 (NH_4)_2S + As_2S_3 + 2 S = 2 (NH_4)_3AsS_4.$$
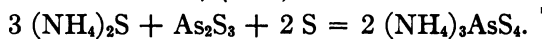
And if this solution be treated with hydrochloric acid, a yellow precipitate of **arsenic pentasulphide** is formed, together with hydrogen sulphide and ammonium chloride:

$$2(NH_4)_3AsS_4 + 6 HCl = As_2S_5 + 3 H_2S + 6 NH_4Cl.$$
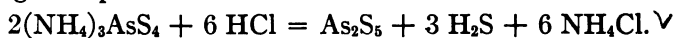
480. Test. (1) In the free condition arsenic may be easily identified by heating a small quantity of the material in a sealed tube. The appearance of the two characteristic forms of arsenic in the colder portion of the tube shows the presence of the element at once.

(2) The substance may be mixed with charcoal and heated in a sealed tube; if much arsenic is present the same deposit will be formed.

Marsh Test for Arsenic

(3) For testing any material for traces of arsenic the **Marsh** apparatus should be used (Fig. 100). This is a hydrogen generator fitted with a thistle-tube, a calcium chloride tube for drying the gas, and a delivery-tube of hard glass. The hydrogen is generated from pure dilute sulphuric acid and pure zinc. Since the generation of the gas is likely to be slow on account of the purity of the reagents, a drop or two of platinum chloride may be added with the acid. After the hydrogen has been escaping for some time the gas is
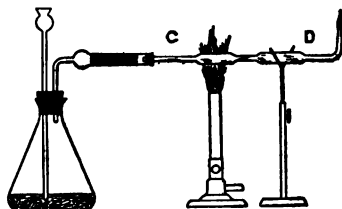
FIG. 100

lighted at D and a burner placed under the delivery-tube at C. The solution of the substance suspected of containing arsenic is then poured into the flask through the funnel-tube. If any arsenic is present, the nascent hydrogen will convert it to the hydride **arsine, AsH₃,** and it will pass over with the excess of hydrogen. As it passes through the hot part of the delivery-tube the arsine will be decomposed into hydrogen and metallic arsenic. The arsenic will appear as a metallic mirror in the cold portion of the hard-glass tube. It is possible by this apparatus to detect quantities of arsenic so small that it is impossible to weigh them. In accurate work it is always necessary to run what is called a "blank test" to make sure that the reagents do not contain any arsenic.

481. Preparation. Arsenic is commonly prepared in the laboratory by heating the trioxide with charcoal:

$$As_2O_3 + 3\,C = 2\,As + 3\,CO.$$
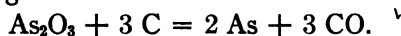
If this is done in a sealed glass tube, the metallic arsenic sublimes in the colder portion of the tube in two distinct layers, the first appearing as a gray, metallic mirror and the second as a black, amorphous deposit. Arsenic could be easily prepared on a large scale by heating the mineral **mispickel,** also known as **arsenopyrite,** in an iron retort.

The arsenic sublimes readily, leaving ferrous sulphide in the retort:

$$4\,FeAsS = 4\,FeS + As_4.$$
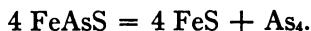
482. Uses. Arsenic is alloyed with lead in the manufacture of shot. The oxide As_2O_3 is used in poisons, in many green paints, and in many insecticides.

483. Compounds of arsenic. Arsenic trioxide, or white arsenic, As_4O_6; arsenic pentoxide, or arsenic anhydride, As_2O_5; arsenious acid, H_3AsO_3; arsenic acid, H_3AsO_4; arsine, AsH_3; sodium arsenite, Na_3AsO_3; arsenic trisulphide, As_2S_3; arsenic pentasulphide, As_2S_5.

484. Arsenic trioxide. This is by far the commonest compound of arsenic. It is known as **white arsenic** and is sold in the drug stores as arsenic. It is also known as **arsenious oxide, or arsenious acid.**

It is formed as a white smoke when arsenic burns in air or oxygen, and when heated is converted directly to the gaseous form without melting. If heated under pressure, it melts to a colorless liquid which solidifies to a glass-like solid. On standing, it changes slowly to an opaque, amorphous variety.

It has a sweet taste and is extremely poisonous. It is used in the preparation of all arsenic compounds.

Antimony

485. Appearance and occurrence. Antimony is a heavy crystalline metal. It occurs in the free condition to some extent, but is found chiefly combined with sulphur as the mineral **stibnite,** Sb_2S_3.

486. Physical properties. When nearly pure, antimony shows on the exposed surface of a freshly cast bar a peculiar fern-like marking. It melts at 632° and boils at 1450°. It is quite brittle and breaks with a distinctly crystalline fracture. Its specific gravity is 6.78.

487. Chemical properties. Antimony burns with a white flame, forming the trioxide Sb_2O_3. This oxide has both basic and acid properties. It dissolves in hydrochloric acid, forming antimony chloride, $SbCl_3$. If the trioxide be boiled with sodium hydroxide, it is converted to **sodium antimonite,** Na_3SbO_3, similar to sodium arsenite.

Antimony unites readily with the halogens forming the tri-halogen compounds:

$$2\ Sb + 3\ Cl_2 = 2\ SbCl_3.$$

If antimony or antimony compounds be boiled with concentrated nitric acid, the antimony is converted to a white, insoluble compound known as **ortho-antimonic** acid. If this acid be heated sufficiently, all of the water may be driven off and the anhydride Sb_2O_5 obtained.

Antimony dissolves slowly in hydrochloric acid with the evolution of hydrogen. It is dissolved readily by aqua regia, forming the trichloride. When antimony trichloride is added to an excess of water it is partly hydrolized and a precipitate of **antimony oxychloride** is formed (250):

$$SbCl_3 + H_2O \rightleftharpoons SbOCl + 2\,HCl.$$
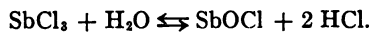
This is a case of a reversible reaction, and it is quite plain that as long as any hydrochloric acid is present it can never be complete. Increase the concentration of the HCl and the precipitate will redissolve.

Hydrogen sulphide produces in solutions of antimony an orange-red precipitate of **antimony trisulphide.**

$$2\,SbCl_3 + 3\,H_2S = Sb_2S_3 + 6\,HCl.$$
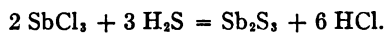
The sulphides of antimony dissolve in colorless and yellow ammonium sulphide, with the formation either of **ammonium thioantimonite,** $(NH)_3SbS_3$, or **ammonium thioantimonate,** $(NH_4)_3SbS_4$, which are compounds perfectly analogous to the corresponding arsenic compounds.

When treated with nascent hydrogen antimony forms the gaseous hydride, SbH_3, called **stibine,** which is similar to arsine.

488. Test. If the substance is in the metallic form, pulverize a small quantity, dissolve it in aqua regia, and evaporate to a very small bulk. Add 1 drop to a large bulk of water. A white cloudy precipitate of the oxychloride shows either antimony or bismuth. Dilute the rest of the solution with water and pass hydrogen sulphide. An orange-red precipitate indicates antimony.

If the substance is a compound, dissolve it in hydrochloric acid, dilute with water, and add hydrogen sulphide; an orange-red precipitate indicates antimony.

489. Uses. Antimony is used in certain alloys, especially type metal:

	Antimony	Tin	Lead	Copper
Type Metal.......	25	25	50	....
Bearing Metal.....	10	85	....	5

490. Compounds. Antimony trioxide, Sb_2O_3; antimony pentoxide, or antimonic anhydride, Sb_2O_5; antimony hydride, or **stibine,** SbH_3; antimony trisulphide, Sb_2S_3; antimony pentasulphide, Sb_2S_5; antimony oxychloride, $SbOCl$.

Bismuth

491. Appearance and occurrence. Bismuth is a heavy, crystalline, brittle metal resembling antimony, but it has a decidedly reddish tint.

The element occurs chiefly in the free condition, but is also found as the trioxide, Bi_2O_3, and the trisulphide, Bi_2S_3.

492. Physical properties. Bismuth melts at $270°$ and boils between $1100°$ and $1300°$. Unlike most metals it expands on solidifying. If the crust which first forms during cooling on the surface of some melted bismuth be broken and the remaining liquid be poured out, the cavity will be found lined with crystals of the metal.

493. Chemical properties. If heated hot enough, bismuth will burn, forming the oxide Bi_2O_3, which is basic. The pentoxide may be made by an indirect method.

Bismuth is not dissolved by hydrochloric acid or cold sulphuric acid. Hot concentrated sulphuric acid reacts with it, however, with the formation of sulphur dioxide:

$$3\ H_2SO_4 = 3\ H_2O + 3\ SO_2 + 3\ O.$$
$$2\ Bi + 3\ O = Bi_2O_3.$$
$$\underline{Bi_2O_3 + 3\ H_2SO_4 = Bi_2(SO_4)_3 + 3\ H_2O.}$$
$$2\ Bi + 6\ H_2SO_4 = Bi_2(SO_4)_3 + 6\ H_2O + 3\ SO_2.$$
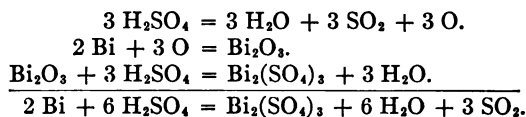
The element is dissolved by nitric acid with the formation of the nitrate $Bi(NO_3)$, which may be crystallized from aqueous solution in white crystals containing 5 molecules of water of crystallization.

Bismuth nitrate is partly hydrolized by an excess of water with the formation of two different basic nitrates:

$$Bi(NO_3)_3 + HOH = Bi\genfrac{}{}{0pt}{}{OH}{(NO_3)_2} + HNO_3.$$

$$Bi(NO_3)_3 + 2\ HOH = Bi\genfrac{}{}{0pt}{}{(OH)_2}{(NO_3)} + 2\ HNO_3.$$
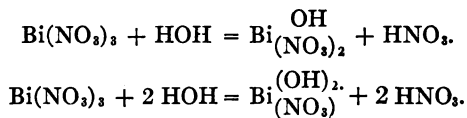
These two compounds are both basic bismuth nitrates, and there is a third which might be considered the same as the second, less 1 molecule of water, $BiO(NO_3)$.

The **subnitrate of bismuth** used in medicine is essentially a mixture of these three basic nitrates.

Bismuth dissolves in aqua regia, forming the trichloride, and the trioxide dissolves in hydrochloric acid, forming the same salt.

If a solution of the trichloride be added to an excess of water, a very voluminous cloudy precipitate of the oxychloride is formed:

$$BiCl_3 + H_2O = \underline{BiOCl} + 2\,HCl.$$
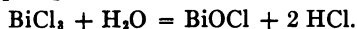
Basic salts. A salt may be considered as an acid in which the hydrogen has been replaced by basic radicals, or as a base in which the OH radical has been replaced by an acid radical. If only part of the hydrogen of a polybasic acid has been replaced, the result is an acid salt. If only part of the OH of a base has been replaced by an acid radical, the result is a basic salt.

494. Test. If the substance is in the solid form, pulverize a small quantity and dissolve it in aqua regia. Evaporate to very small bulk and add 1 drop to a large quantity of water. A white, cloudy precipitate shows either bismuth or antimony. Dilute the rest of the solution with water and pass in hydrogen sulphide. A black precipitate indicates bismuth.

FIG. 101

If the substance is a compound, dissolve a small quantity in hydrochloric acid, dilute with water, and pass in hydrogen sulphide. Filter off the black sulphide and dissolve it in aqua regia. Concentrate to small bulk and add 1 drop to a large volume of water. A white, cloudy precipitate is the oxychloride of bismuth.

495. Preparation. Bismuth may be prepared by roasting the sulphide, Bi_2S_3, which converts it to the oxide, Bi_2O_3, and reducing the latter with carbon:

$$Bi_2O_3 + 3\,C = 2\,Bi + 3\,CO.$$
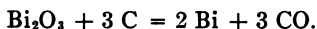
496. Uses. Bismuth in the metallic form is used as an ingredient of many alloys. The following table gives the approximate proportions of the ingredients in the more common ones.

Name	Bismuth	Tin	Lead	Cadmium	Melting-Point
Wood's metal.......	40	12.5	25	12.5	60° C.
Rose's metal........	50	25	25	....	93.75° C.
Lipowitz's metal....	50	13.3	26.7	10	158° C.

These alloys are used in automatic sprinklers (Fig. 101), for solders where it is important that the temperature should not be raised above the boiling-point of water, and for small, hollow statuettes.
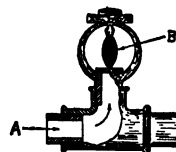
497. Compounds. Bismuth trioxide, Bi_2O_3; **bismuth hydroxide,** $Bi(OH)_3$; bismuth trichloride, $BiCl_3$; **bismuth oxychloride,** $BiOCl$; bismuth nitrate, $Bi(NO_3)_3$; basic bismuth nitrates contained in the **sub-nitrate,** $BiOH(NO_3)_2$, $Bi(OH)_2NO_3$, and $BiONO_3$; **bismuth trisulphide,** Bi_2S_3; bismuth sulphate, $Bi_2(SO_4)_3$.

CHAPTER XXXIII

CARBON

(Laboratory Exercise No. 26)

498. Appearance. Carbon exists in three different modifications, known as diamond, graphite, and amorphous carbon. The diamond is crystalline and transparent and those most seen are perfectly colorless; but blue, green, red, olive, black, and yellow varieties are known. Graphite is also crystalline but grayish-black in color and non-transparent. Amorphous carbon occurs in a great many forms more or less familiar. Lampblack, wood-charcoal, coal, gas-carbon, and coke are all examples of this variety.

499. Occurrence. Carbon in the form of coal is found in large quantities all over the world. Graphite, or plumbago, occurs in limited quantities and is mined in California, Ceylon, and Siberia. Diamond, the purest and rarest form of carbon, is mined in South Africa and Brazil. A small sketch of the largest diamond ever found, the *Cullinan*, is shown in Fig. 102. It was found in South Africa in 1905. Before cutting, it was as large as a man's fist and weighed over 3,000 carats.

Fig. 102

In combination with oxygen, carbon exists in the air as carbon dioxide to the extent of 3 parts in 10,000 by volume. It is an important constituent of all animal and vegetable tissue, in which it exists in combination with hydrogen, oxygen, and nitrogen in a large variety of definite chemical compounds. Petroleum and natural gas are made up of a large number of compounds of carbon and hydrogen. All of the natural rocks known as carbonates, especially limestone and marble, are compounds of carbon.

500. Diamond. Diamond is usually colorless, and is the hardest substance known. It has a very high refractive power,

as a result of which it can be cut in such shapes that all of the light falling upon it is reflected again, rendering it very brilliant.   It has a specific gravity of 3.5.   When heated in air or oxygen it burns completely, forming carbon dioxide.   If .12 g. of diamond be burned in an excess of oxygen, exactly .44 g. of carbon dioxide will be formed.   Since 12 weights of carbon form 44 weights of carbon dioxide, this proves that the diamond contains nothing but carbon.   When heated sufficiently out of contact with oxygen or air, diamond becomes pasty and is converted to graphite.

Aside from its use in jewelry and ornaments, the diamond is used in cutting other diamonds and precious stones.   It is also used for the bearings in delicate pieces of mechanism where it is undesirable that there should be any wear whatever. A cheap form of black diamond is used in diamond drills.   These drills consist essentially of an iron pipe, the cutting edge of which is studded with diamonds.   As the pipe revolves, the diamonds cut their way into the rock, allowing a cylindrical core to enter the pipe.   From time to time this cylindrical piece of rock is withdrawn from the hole and shows perfectly what kind of material the drill is passing through.

501. Graphite.   Graphite is a grayish-black solid found in both the crystalline and amorphous conditions.   It has a specific gravity of 2.25 and is very soft.   When heated in an atmosphere of oxygen it burns with great difficulty, forming carbon dioxide.   Like the diamond, .12 g. of graphite produce .44 g. of carbon dioxide, which shows that the substance contains nothing but carbon.

It is used in the manufacture of lead-pencils, crucibles, and stove-blacking.   On account of its low coefficient of friction it is of great value as a lubricant on bearings where either the pressure or the temperature are too high to admit of the use of oil.

Artificial graphite is now manufactured in large quantities in the electric furnace and is very extensively used for electrodes in the manufacture of many electrolytic products.

Amorphous Carbon

502. Coal.   Coal-beds are the fossil remains of luxuriant tropical forests of a past geological age.   This carboniferous

material has been gradually decomposed through thousands of years, giving off water and compounds of carbon and hydrogen. The weight of additional layers of earthy matter, with the pressure due to the shrinkage of the earth's crust and the internal heat of the earth, have combined to convert these vegetable remains to the different forms of coal that we have to-day.

The different forms of fuel containing carbon as the chief combustible element are given in the following table:

	Percentage of Carbon	Volatile Hydrocarbons, Water, and Ash
Wood......................	45	55
Peat......................	55	45
Brown coal................	67	33
Soft coal.................	80	20
Cannel coal...............	85	15
Anthracite................	94	6
Charcoal..................	95	5
Coke......................	96	4

Soft coal, also called bituminous coal, besides the carbon, contains a large quantity of volatile hydrocarbons, which distil from the burning coal and burn with a smoky flame, giving off large quantities of soot. Cannel coal is a variety of bituminous coal so rich in combustible hydrocarbons that it may be ignited directly with a match.

Anthracite is a very dense variety of coal, containing almost no volatile hydrocarbons and burns almost without flame and produces no smoke.

503. Charcoal. Charcoal is made by heating wood sufficiently to drive off all of the water and volatile products. This is done in two different ways. In the older method the wood is piled in circular heaps and covered with sod. The pile is then ignited and only a limited amount of air admitted. The burning of some of the wood heats all of the rest in the heap sufficiently to drive off all of the volatile products (Fig. 103).

This method is wasteful, for all of the volatile products. some of which are of more value than the charcoal, are lost.
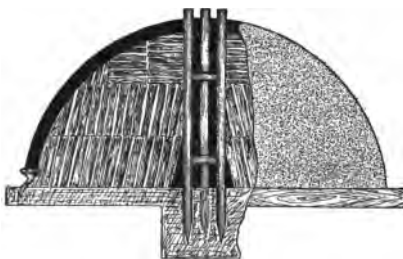
Fig. 103

In the more modern process the wood is heated in large iron retorts and all of the volatile products are recovered (Fig. 104). Among these products are creosote, acetic acid, wood-alcohol, and a combustible gas which is itself burned under the retorts.

504. Animal charcoal is made by subjecting all kinds of animal matter to destructive distillation in iron retorts.

Freshly prepared charcoal has a great tendency to absorb gases of all kinds. This condensation of gases is always accompanied by an increase of temperature, and it is quite possible for charcoal to burst into flame spontaneously, especially if any combustible gas has been absorbed as well as the oxygen of the air. This absorption of gases by charcoal is due to the adhesion between the molecules of the gas and the very large surface rendered available by the porosity of the charcoal. Since it is a process due partly to adhesion and absorption, it is called **adsorption**.

Charcoal also has the power to remove certain organic colors and bitter tastes from liquids. Hydrogen sulphide water, colored with litmus solution and made bitter with a small quantity of quinine, when boiled with charcoal and filtered, is rendered colorless, odorless, and tasteless. Charcoal is much used in the purification of sugar syrup in sugar refineries.
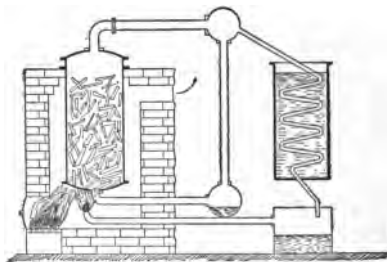
Fig. 104

505. Coke and gas carbon.
Coke bears the same relation to bituminous coal that charcoal does to wood. It is made by heating soft coal sufficiently to

drive off all of the volatile products. In the older process, the coal is placed in a large oven shaped like a beehive (Fig. 105). It is then set on fire and nearly all of the air supply shut off. The burning of some of the coal furnishes enough heat to convert the rest to coke. The volatile products escape from the top of the oven and burn with a ruddy flame. This process, like the older method of making char-coal, is very wasteful of the valuable by-products and is rapidly being replaced by processes in which the coal is heated in large retorts and all of the volatile products recovered. Among the products obtained in the by-product method of making coke are ammonia, benzol, and fuel gas. The fuel gas is used for heating the retorts as well as for generating steam and running gas-engines at the works. Coke has also been obtained for years as a by-product in the manufacture of illuminating gas by the destructive distillation of soft coal.
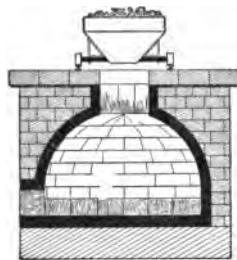
Fig. 105

Coke is very free from sulphur and is much used in the reduction of iron ores.

Gas carbon. Gas carbon is a very dense variety of carbon which accumulates in the retorts used in the manufacture of illuminating gas by the distillation of soft coal.

506. Lampblack. Lampblack is formed by allowing a smoky flame of a burning hydrocarbon gas to play on a cool surface. It is a very finely divided black powder much used in the manufacture of printer's ink.

507. Physical properties of carbon. Under the action of the electric current carbon can be converted to a pasty condition. No liquids dissolve it under ordinary conditions. It is, however, soluble in molten iron, from which on cooling it separates in the crystalline form. Its molecule is supposed to contain a large number of atoms.

508. Chemical properties of carbon. All forms of carbon combine directly with oxygen when ignited sufficiently, forming carbon dioxide:

$$C + O_2 = CO_2.$$
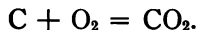
If there is a great excess of carbon present, or the CO_2 that is at first formed is compelled to pass over hot carbon, a colorless gas called carbon monoxide is given off. This is really formed by the reduction of the dioxide by carbon:

$$CO_2 + C = 2\,CO.$$

On account of its attraction for oxygen, carbon will remove the oxygen from many substances when heated with them. It is therefore a reducing agent and is extensively used for the reduction of metallic oxides:

$$C + 2\,CuO = CO_2 + 2\,Cu.$$
$$3\,C + 2\,Fe_2O_3 = 3\,CO_2 + 4\,Fe.$$
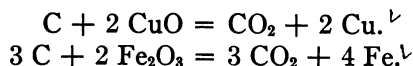
If steam be passed over white-hot carbon the water is reduced to hydrogen, and carbon monoxide is formed. This mixture of hydrogen and carbon monoxide is known as **water-gas:**

$$C + H_2O = H_2 + CO.$$

When charcoal is boiled with concentrated sulphuric acid, the acid is reduced to sulphurous acid, which breaks up into water and sulphur dioxide, and carbon dioxide is formed:

$$C + 2\,H_2SO_4 = 2\,H_2O + 2\,SO_2 + CO_2.$$

In each of the above cases carbon was the reducing agent and the other substance the oxidizing agent.

At the temperature of the electric furnace carbon unites directly with many metals, forming carbides. The two most important of these carbides are **silicon carbide,** SiC, also known as **carborundum,** and **calcium carbide,** CaC_2.

Sulphur vapor passed over very hot carbon combines with it directly, forming **carbon disulphide,** CS_2.

509. Test. It is usually sufficient to burn the substance in oxygen or air and cause the products to come in contact with lime-water or barium hydroxide. The formation of a white precipitate of the carbonate shows the presence of carbon. In the case of many organic substances the presence of carbon is apparent at once on heating.

510. Preparation. Pure carbon may readily be prepared by heating pure sugar to a high temperature out of contact with the air.

511. Uses. Some of the uses have already been referred to. In addition to its universal use for the production of heat it is used as a reducing agent; for the purification and decolorization of liquids; for the preparation of many binary compounds and the manufacture of printer's ink.

512. Common compounds. Carbon dioxide, or carbonic acid gas, CO_2; carbon monoxide, or coal-gas, CO; carbon disulphide, CS_2; methane, or marsh-gas, CH_4; chloroform, $CHCl_3$; carbonic acid, H_2CO_3; sodium carbonate, Na_2CO_3; calcium carbonate, limestone or marble, $CaCO_3$; methyl hydroxide, or wood-alcohol, CH_3OH; ethyl hydroxide, or common alcohol, C_2H_5OH; sugar, $C_{12}H_{22}O_{11}$; cellulose, or cotton, $C_6H_{10}O_5$.

CHAPTER XXXIV

OXIDES OF CARBON

Carbon Dioxide (Laboratory Exercise No. 27)

513. Appearance and occurrence. Carbon dioxide is a heavy colorless gas with a slight odor and sour taste. It occurs free in the atmosphere, of which it forms about 3 parts in 10,000 by volume. It is given off by certain effervescent spring-waters and issues from the ground in large volume in some localities in the world. It is also exhaled by all breathing animals, and is formed by the burning of any substance containing carbon.

514. Physical properties. Under ordinary conditions at constant pressure, a volume of carbon dioxide gas varies directly as its absolute temperature (Charles's law), and at constant temperature it varies inversely as the pressure (Boyle's law). The gas can be condensed to the liquid by pressure and cold. Its critical temperature is 31.1°. This is the temperature above which no amount of pressure will cause the gas to become liquid. If a strong glass tube three quarters full of liquid carbon dioxide be slowly warmed by the heat of the hands, the liquid will begin to boil and the meniscus showing the surface of the liquid will slowly fall until at 31.1° it will disappear entirely. On cooling the tube a little below the critical temperature condensation takes place at once and the dividing line between the liquid and the gas again appears. The pressure just sufficient to cause a gas to change to a liquid at its critical temperature is called the **critical pressure.** When any liquid is converted to the gaseous form a large quantity of heat is absorbed. If the evaporation takes place spontaneously, the temperature of the liquid falls. This is very noticeable when the liquid is one that has been condensed from the gaseous condition by great pressure. Liquid carbon dioxide evaporates so rapidly when the pressure is removed that some of it is converted to the solid form. **Solid carbon dioxide** may be easily prepared by fastening a stout cloth bag over the outlet of a cylinder of the liquefied gas (Fig. 106), inverting the cylinder so the liquid is in contact with the valve, and opening the valve carefully. The rapid expansion of the gas produces so much cold that some of the liquid is

FIG. 106

solidified, and the bag is soon filled with a snow-like, solid mass. This solid mixed with ether gives a very low temperature, about −80°, and forms a very convenient freezing mixture for the laboratory. Other liquids, such as alcohol or benzine, may be used in place of ether with equally good results.

515. Chemical properties. Carbon dioxide does not burn or support the combustion of ordinary substances. Sodium, potassium, and magnesium when ignited and thrust into the gas continue to burn, reducing the gas to carbon:

$$2 \, Mg + CO_2 = 2 \, MgO + C.$$
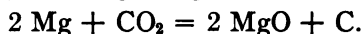
The gas is the anhydride of carbonic acid, a weak and unstable acid which exists only in solution:

$$CO_2 + H_2O \leftrightarrows H_2CO_3.$$
$$a \qquad b \qquad c$$
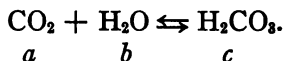
This is a reversible reaction, according to the **law of mass action (235)**—the ratio of the products of the concentrations of the factors to the product of the concentrations of the products is equal to a constant. Therefore $\dfrac{a \times b}{c} = k$. If the solution be boiled, some of the CO_2 escapes, the concentration of the CO_2 is lessened, and therefore some of the acid decomposes in order to maintain the equilibrium. All of the carbonic acid may be removed by boiling.

On the other hand, if the solution of the gas in water is made under pressure, the concentration of the carbon dioxide is very much greater, and the concentration of the carbonic acid is much increased. If the pressure is suddenly removed, the rapid escape of the gas produces an effervescence:

Carbon dioxide unites directly with alkalies and alkaline oxides to form carbonates and bicarbonates:

$$2 \, NaOH + CO_2 = Na_2CO_3 + H_2O.$$
$$CaO + CO_2 = CaCO_3.$$
$$Ca(OH)_2 + 2 \, CO_2 = CaH_2(CO_3)_2.$$
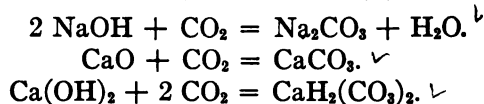
If an excess of carbon dioxide be passed into a sodium hydroxide solution the acid salt is formed, $HNaCO_3$. This is called **acid sodium carbonate, hydrogen sodium carbonate,** or **bicarbonate of soda.**

516. Test. Carbon dioxide is usually recognized by the fact that it produces a white precipitate of calcium carbonate in lime-water or of barium carbonate in barium hydroxide:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$
$$Ba(OH)_2 + CO_2 = \overline{BaCO_3} + H_2O.$$
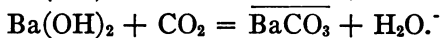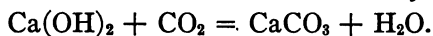
517. Preparation. Carbon dioxide is commonly made in the laboratory by the action of an acid on a carbonate. While all of the carbonates react with the common acids, calcium carbonate, in the form of broken marble, and hydrochloric acid, on account of their small cost, are the reagents best adapted to the preparation of the gas:

$$CaCO_3 + 2\,HCl = CaCl_2 + H_2O + CO_2.$$

Any form of gas generator will do, but for the preparation of the gas on a small scale in the laboratory a wide-mouth bottle
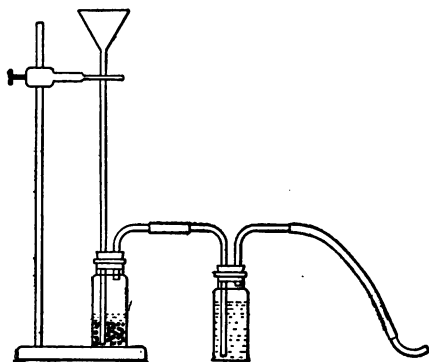
. FIG. 107

with a two-hole stopper fitted with a funnel-tube and delivery-tube is all that is necessary. The acid is added through the funnel-tube as the gas is required (Fig. 107).

There are few products made by the pupil in the laboratory which are absolutely pure as first made. It is the pupil's duty to consider what impurities may be present and to devise means for removing them, even if the process is not put into practical operation. In the case of the preparation of a gas by a reaction accompanied by effervescence, the gas is always contaminated by a spray of the liquid, which is carried over into the receiver mechanically mixed with the gas.

In the above case the mechanical impurities would be water, calcium chloride, and hydrochloric acid. The two latter of these impurities could be removed largely by causing the gas to bubble through some water in a second bottle. If it were

necessary to remove the water also, the gas could be passed through concentrated sulphuric acid in a third bottle or a tube filled with dry calcium chloride.

Carbon dioxide is manufactured on an enormous scale by the action of acids on marble dust, and sold in the liquid form in large iron cylinders.

The natural gas obtained from effervescing springs, as well as that obtained from the fermentation of beer in breweries, is also sold in the liquid form.

The carbon dioxide used in the manufacture of carbonate of soda by the ammonia process is taken entirely from the lime-kilns. Here it is formed partly by the burning of coke and partly from the limestone which gives it off when heated:

$$C + O_2 = CO_2.$$
$$CaCO_3 \text{ heated} = CaO + CO_2.$$
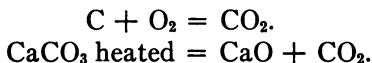
When bicarbonate of soda is heated it gives off water and carbon dioxide:

$$2 HNaCO_3 = Na_2CO_3 + H_2O + CO_2.$$

518. Uses. Carbon dioxide is used in the manufacture of all kinds of effervescing beverages. The water of the soda fountain and the syphon (Fig. 108) is simply water containing carbon dioxide under pressure. It is used in fire-extinguishers and chemical engines, where it is generated just before use by the action of sulphuric acid on bicarbonate of soda (Fig. 109).
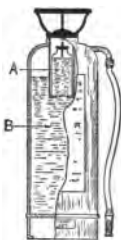
It is also used for the preparation of sodium carbonate and bicarbonate.

FIG. 108

519. Carbonic acid. This acid, having the formula H_2CO_3, has already been referred to as an unstable acid existing in solution. When the pressure is removed or the solution is boiled it splits into water and the anhydride. It is a weak acid, being very slightly ionized in solution.

FIG. 109

520. Carbonates. Carbonates are the salts of carbonic acid and are very well-known and stable compounds. Carbonates of nearly all of the metals are known, the most common being calcium carbonate, $CaCO_3$, in the form of limestone or marble, and sodium carbonate, Na_2CO_3, in the form of **soda ash,** or **sal soda.**

All of the carbonates except those of the alkali metals give up carbon dioxide when heated:

$$MgCO_3 = MgO + CO_2.$$

The carbonates of the alkali metals melt quietly without evolution of CO_2.

A water solution of sodium or potassium carbonate reacts alkaline. Water itself is neutral, because the hydrogen and hydroxide ions are present in exactly the same quantities. When the carbonate is dissolved some of the CO_3 ions form undissociated carbonic acid with some of the hydrogen ions, leaving an excess of hydroxide ions:

$$Na_2CO_3 + H^+ + H^+ + OH^- + OH^- \leftrightarrows H_2CO_3 + Na^+ + Na^+ + OH^- + OH^-.$$
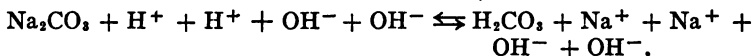
Carbon Monoxide

521. Appearance. Carbon monoxide is a colorless gas that burns with a characteristic blue flame which is always seen when a fresh supply of coal is put on a hot fire.

522. Physical properties. Under ordinary conditions its volume changes according to Boyle's and Charles's laws. With sufficient pressure and cold it may be condensed to a liquid and the liquid may be solidified. Its critical temperature is $-139.5°$ and its critical pressure is 35.5 atmospheres. It is very slightly soluble in water.

523. Chemical properties. It burns readily in oxygen or air, forming carbon dioxide. 2 volumes of the gas exactly unite with 1 volume of oxygen, forming 2 volumes of CO_2:

$$2 CO + O_2 = 2 CO_2.$$
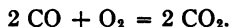
The gas is a powerful reducing agent and at a high temperature will remove the oxygen from metallic oxides, setting the metal free. In the blast-furnace the charcoal or coke is first burned to carbon dioxide. This, in passing over hot carbon, is reduced to carbon monoxide, which in turn unites with the oxygen of the iron ore:

$$Fe_2O_3 + 3 CO = 2 Fe + 3 CO_2.$$

Carbon monoxide is a powerful poison, on account of its ability to form a stable compound with the hæmoglobin of the blood, thereby preventing the blood from absorbing oxygen or removing the carbon dioxide. A very small amount is sufficient to produce death.

It is always present in illuminating gas, and is given off when a fresh supply of coal is put on a hot fire. Great care should be exercised in closing the dampers of a coal stove or furnace for the night to see that there is sufficient draught left to prevent any products of combustion from escaping into the room.

Test. There is no simple chemical test for the gas. It is mechanically absorbed by a solution of cuprous chloride in hydrochloric acid.

524. Preparation. In the laboratory the gas is sometimes made by boiling oxalic acid with sulphuric. Carbon dioxide is formed at the same time and must be removed by passing the mixed gases through sodium or potassium hydroxide:

$$C_2H_2O_4 = CO_2 + CO + H_2O.$$

It is manufactured on a large scale mixed with nitrogen in the form known as **producer gas** by drawing or blowing air through a hot coal fire kept smothered with coal (Fig. 110). Producer gas is much used in a great variety of manufacturing industries as a convenient and efficient means for the distribution of heat and power to different parts of the works.

FIG. 110

It is also manufactured mixed with hydrogen in the form of water-gas by blowing steam through white-hot coal. This reaction is accompanied by the absorption of much heat and at frequent intervals the steam is shut off and a blast of air turned on to reheat the coal (**544**):

$$C + H_2O = CO + H_2.$$
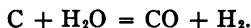
525. Uses. Producer gas and water-gas are used to run gas-engines, and for furnishing heat. Water-gas is enriched with various hydrocarbon gases and constitutes much of the illuminating gas used to-day (**543**).
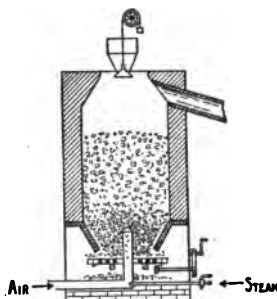
CHAPTER XXXV

The Raising of Bread

Bread. By "bread" is meant any combination of flour with other substances which is to be cooked. This includes cake and puddings of all sorts.

526. Flour. Flour is composed largely of starch and gluten. When flour is worked up with a plentiful supply of water the starch soon separates as a deposit in the vessel, and the gluten collects in one lump as a sticky mass. In order to produce a light loaf it is quite necessary to get the mass of flour and water full of small bubbles of air or harmless gas before the baking. This may be accomplished in various ways.

527. Mechanically aerated bread. The mixture of flour, water, and salt may be thoroughly beaten, thereby filling it with minute bubbles of air which are mechanically held by the gluten. When such bread is baked each small bubble of air expands with the heat and the loaf rises.

The flour mixture may be put into a special apparatus and beaten in an atmosphere of carbon dioxide under pressure. Again the bubbles of gas are held by the gluten, and when the loaf is baked the expansion of the gas produces the necessary expansion of the loaf.

528. Salt-raised bread. This term is applied to bread that is raised by means of fermentation, but without the use of yeast. The process is about as follows: some milk is sterilized by heating nearly to boiling and mixed to a stiff batter with corn-meal flour. This mixture is covered and placed where its temperature will remain at about blood-heat for several hours until active fermentation has set in.

The salt, mixed with hot milk and flour, is then worked into the mass of fermented material and again set aside in a warm place.

356

The whole mass is then worked into the proper quantity of flour to make the finished loaves. After standing until they have swelled to the required size the loaves are baked.

529. Yeast. The yeast-plant consists of a collection of small cells forming a slimy yellow mass. This plant grows with great rapidity provided the temperature is right and there is enough fermentable sugar and nitrogenous matter present. The yeast-plant is filtered off, mixed with starch and flour, and sold in the form of compressed yeast. The yeast when mixed with the flour has the power of converting the starch to sugar and the sugar to alcohol and carbon dioxide. When the bread is baked the bubbles of carbon dioxide expand and raise the loaf.

Baking-Powders (Laboratory Exercise No. 28)

530. Baking-powder. When very quick results are desired, baking-powder is incorporated in the dough. Baking-powders all consist of a mixture of sodium bicarbonate with a dry powdered acid, an acid salt, or a salt that reacts acid, mixed with a little starch to prevent deterioration. When the mixture is moistened carbon dioxide is liberated and produces the necessary bubbles of gas in the loaf.

531. Cream-of-tartar powder. This powder consists of a mixture of cream of tartar (acid potassium tartrate) and sodium bicarbonate in molecular proportions, as shown by the following equation:

$$HKC_4H_4O_6 + HNaCO_3 = NaKC_4H_4O_6 + CO_2 + H_2O.$$
$$188 84 210 44 18$$

It is apparent that, as a result of the use of this powder, the chemical compound $NaKC_4H_4O_6$, known as **Rochelle salt**, is left in the cake or bread. This substance, however, has no undesirable physiological action and might be considered beneficial.

532. Tartaric acid powder. This powder would be just as good as the cream-of-tartar powder, but it is not manufactured to any great extent. Its composition is shown by the equation:

$$H_2C_4H_4O_6 + 2\,HNaCO_3 = Na_2C_4H_4O_6 + 2\,CO_2 + 2\,H_2O.$$
$$150 168 194 88 36$$
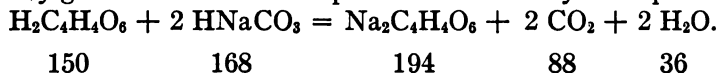
Here the chemical compound left in the cake is normal sodium tartrate, $Na_2C_4H_4O_6$. This is also harmless.

533. Acid phosphate powder. In this powder 1 molecule of monocalcium phosphate is mixed with 2 molecules of sodium bicarbonate, and the action of the powder is shown by the equation:

$$H_4Ca(PO_4)_2 + 2\ HNaCO_3 = HCaPO_4 + HNa_2PO_4 + 2\ CO_2 +$$

$$234 \qquad\qquad 168 \qquad\qquad 136 \qquad\quad 142 \qquad\quad 88$$

$$2\ H_2O.$$

$$36$$
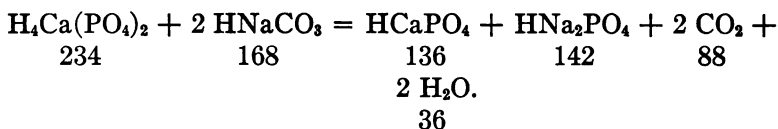
The compounds left in the food by the use of this powder are dicalcium phosphate, $HCaPO_4$, and hydrogen disodium phosphate, HNa_2PO_4. Each of these compounds is supposed to be beneficial rather than otherwise in the quantities that would be taken with the food.

534. Alum powder. Alum is a double sulphate of either ammonium sulphate or potassium sulphate with aluminum sulphate and contains 24 molecules of water of crystallization. The whole formula of ammonium alum would be $(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 + 24\ H_2O$. A water solution of an alum reacts acid and will liberate carbon dioxide from a carbonate. The acid reaction is due to the aluminum sulphate alone, which is a salt of a strong acid with a weak base.

Aluminum sulphate is hydrolyzed by water, forming some free sulphuric acid and aluminum hydroxide (**250**):

$$Al_2(SO_4)_3 + 6\ HOH \rightleftharpoons 2\ Al(OH)_3 + 3\ H_2SO_4.$$
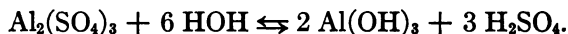
This reaction is reversible and does not proceed far enough to show a precipitate of the hydroxide. Nevertheless, if a carbonate is present to neutralize the acid, the equilibrium is destroyed and the reaction goes on to completion. 1 molecule of aluminum sulphate, therefore, or its equivalent, 1 molecule of alum, will require 6 molecules of bicarbonate of soda to neutralize it.

The alum is usually "burned," that is, heated until all of the water is driven off, and it becomes a dry white powder. An equation showing the composition and action of a typical alum powder follows:

$$(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 + 6\ HNaCO_3 = 2\ Al(OH)_3 + 3\ Na_2SO_4 +$$
$$\ 475 504 157 426$$
$$(NH_4)_2SO_4 + 6\ CO_2.$$
$$132 264$$
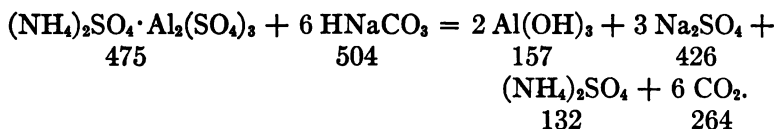
It is apparent that the chemical compounds which must be eaten with food prepared with the use of this powder are aluminum hydroxide, $Al(OH)_3$; sodium sulphate, Na_2SO_4; and ammonium sulphate, $(NH_4)_2SO_4$. Small quantities of sodium sulphate are harmless, but there seems to be some question whether the other two substances are desirable or not.

CHAPTER XXXVI

Hydrocarbons

535. Paraffine series. Carbon forms a very large number of compounds with hydrogen, known as hydrocarbons. When these compounds are classified according to the relative numbers of carbon and hydrogen atoms in the molecule and the members of each class are arranged according to their increasing molecular weights, we have a series each member of which differs from the preceding by a certain fixed weight.

The first series, beginning with the compound **methane, or marsh-gas,** and the higher members of which constitute the **paraffines,** is known as the **marsh-gas** or **paraffine series:**

CH_4, methane, or marsh-gas.

C_2H_6, ethane.

C_3H_8, propane.

C_4H_{10}, butane.

C_5H_{12}, pentane.

$C_nH_{(2n + 2)}$.

Each member of this series differs from the preceding by the group CH_2. The carbon atoms, at least of the lower members, are joined together in a chain. Each carbon atom except the end ones is in combination with 2 hydrogen atoms, and the end ones with 3. This is best shown by a graphic formula:

$$
\begin{array}{ccc}
H & H & H \\
| & | & | \\
H-C-C-C-H \\
| & | & | \\
H & H & H
\end{array}
$$
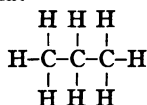
It is plain that in such a compound there will always be as many hydrogen atoms as twice the number of carbon atoms plus 2; hence the general formula

$$C_nH_{(2n + 2)}.$$

536. Methane. Methane, or marsh-gas, is a colorless gas that burns with a slightly luminous flame. It gets its name from the fact that it is formed by vegetable decay and rises to the surface in considerable quantity when the bottom of a marsh or pond is disturbed (Fig. 111).

It is also frequently encountered in coal-mines and when mixed with air forms an explosive mixture called **fire-damp.**

When it burns, carbon dioxide and water are formed:

$$CH_4 + 2 O_2 = CO_2 + 2 H_2O.$$
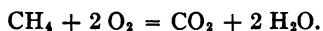
It may be prepared in the laboratory by the dry distillation of a mixture of sodium acetate and sodium hydroxide:

$$NaC_2H_3O_2 + NaOH = Na_2CO_3 + CH_4.$$

537. Hydrocarbon derivatives. It is possible to substitute other atoms or groups of atoms for one or more of the hydrogen atoms in a hydrocarbon.

If methane be treated with chlorine under the proper circumstances, compounds having the formulas CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4 may be formed. CH_3Cl is called monochlormethane; CH_2Cl_2 dichlormethane; $CHCl_3$ trichlormethane, or **chloroform**; and CCl_4 would be tetrachlormethane, or carbon tetrachloride.

538. Unsaturated hydrocarbons. The hydrocarbons referred to above are all saturated compounds—that is, they each contain all the hydrogen the valence of the carbon calls for and are incapable of combining directly with anything else. Hydrocarbons that can combine directly with other elements are called unsaturated. The following series, called the **ethylene** series, is made up of unsaturated hydrocarbons and each member can combine with two equivalents of other elements:
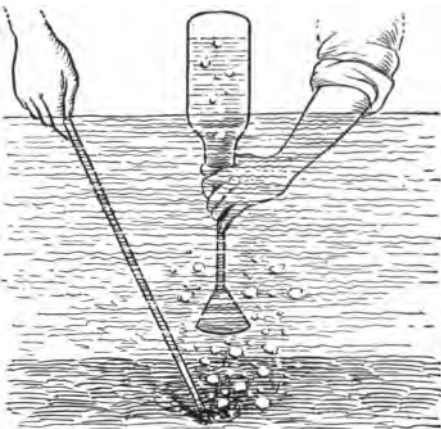
FIG. 111

C_2H_4, ethylene.
C_3H_6, propylene.
C_4H_8, butylene.
C_5H_{10}, amylene.
C_6H_{12}, hexylene.
C_nH_{2n}.

539. Ethylene. Ethylene is a colorless gas that burns with a luminous flame. It is a constituent of illuminating gas and may be prepared by the action of concentrated sulphuric acid upon alcohol:

$$C_2H_5OH - H_2O = C_2H_4.$$

The sulphuric acid acts as a dehydrating agent and extracts one molecule of water.

540. Acetylene. Acetylene is a colorless gas with a peculiar odor, which burns with an intense white light. It is easily prepared by the action of water on calcium carbide:

$$CaC_2 + 2 H_2O = C_2H_2 + Ca(OH)_2.$$
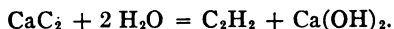
It is used as an illuminant for bicycle and automobile headlights and for lighting buildings out of the range of gas or electric plants (Figs. 112 and 113).
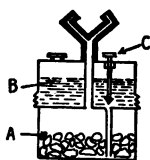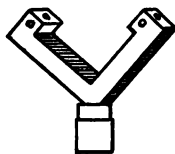
FIG. 112   FIG. 113

541. Coal-Gas. Coal-gas is made by heating soft coal in large retorts made of fire-clay. The general arrangement of a coal-gas plant is indicated in the following sketch (Fig. 114).

The coal is placed in the retort, *F*, which is heated by the fire, *B;* the volatile products pass up into the hydraulic main, *A*. From here the gas is forced into the condenser, *E*, where it is cooled and the tar condensed. The tar passes into the tar-well, *H*. After leaving the condenser the gas passes through the scrubber, *D*, where it filters through a large mass of coke over which water is constantly trickling. The water absorbs all of the ammonia which is present, partly in the free condition and partly as ammonium carbonate and ammonium sulphide. The water from the scrubber constitutes the **ammoniacal liquor**
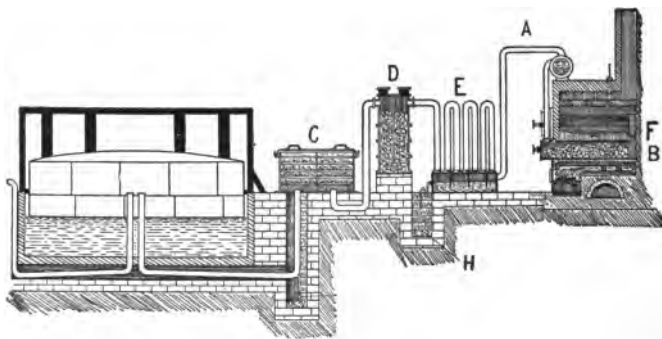
FIG. 114

of the gas-works and is the source of a large proportion of the ammonia and ammonium compounds of commerce.

The gas finally goes through the purifiers, C, which contain a mixture of shavings and ferric oxide, to remove the carbon dioxide and hydrogen sulphide.

542. Composition of coal-gas. The most important constituents of coal-gas are given in the following table:

Coal-Gas			Carburetted Water-Gas
Hydrogen	H_2,	about 49%	30%
Marsh-gas.	CH_4,	" 34%	20%
Carbon monoxide. . .	CO,	" 7%	28%
Nitrogen.	N_2,	" 3%	4%
Ethylene.	C_2H_4,	" 3%	11%
Carbon dioxide.	CO_2,	" 1%	2.5%
Other hydrocarbons and impurities. . . .		3%	4.5%

543. Water-gas. Water-gas has already been mentioned. It is made by blowing steam over very hot anthracite coal or coke. The reaction is as follows:

$$H_2O + C = CO + H_2.$$
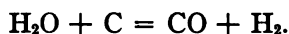
While this gas has a high fuel value, it burns with an almost colorless flame, giving little or no light. In order that the gas may be used for illuminating purposes, it is enriched by spraying mineral oil into a very hot part of the apparatus called the **carburetor.** The heat breaks the oil into permanent gases which give the water-gas illuminating power.

The process is intermittent, for the reason that heat is absorbed in decomposing the water, and from time to time an air-blast must be turned on the fire to bring it again to a white heat.

544. Manufacture of carburetted water-gas. A plant for the manufacture of carburetted water-gas constitutes a part of many gas-works. The product is always mixed with coal-gas before going out into the street mains. The following sketch shows the general arrangement of such a plant (Fig. 115).

The operation consists of two steps: first, the valve at the top of the superheater is opened and a blast of air driven in
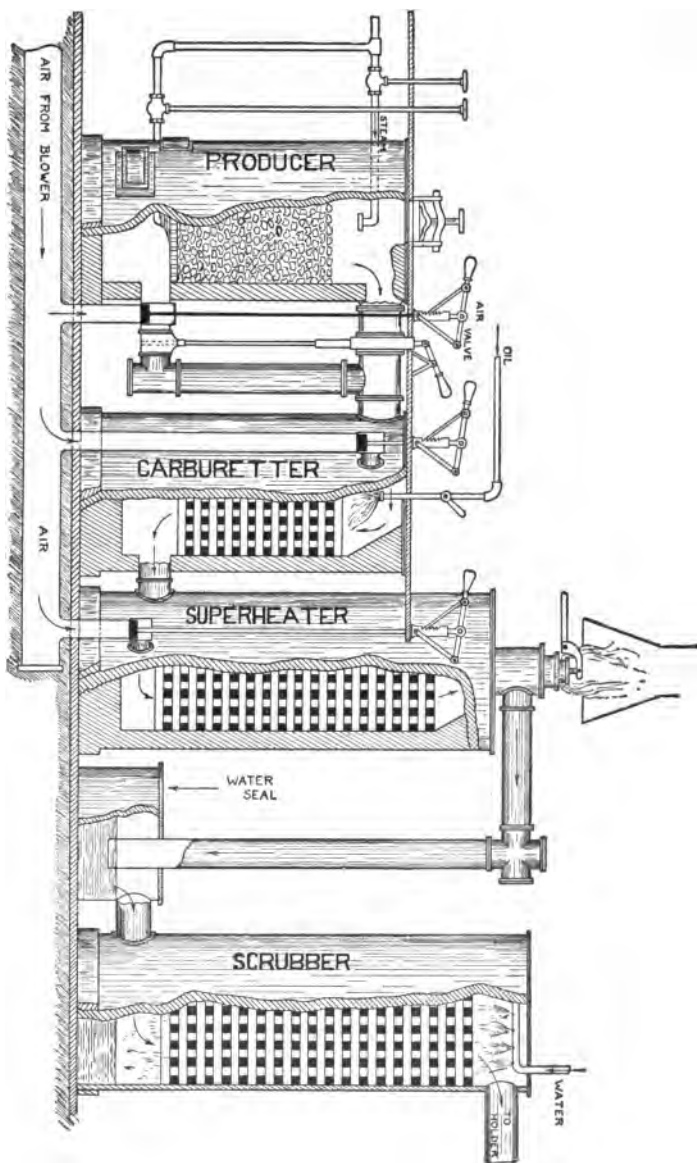
FIG. 115. PLANT FOR MAKING CARBURETTED WATER-GAS. (From plans furnished by the New Haven Gas Co.)

at the bottom of the producer. This generates producer gas, which passes out through the top of the producer and into the top of the carburetor.

At this point more air is admitted in sufficient quantity to completely burn the gas. This results in a blue flame, which goes down through a mass of checker-work of fire-brick in the carburetor and up through similar checker-work in the super-heater. When the checker-work in both the carburetor and the superheater is raised to a sufficiently high temperature, usually in about five minutes, the blast is shut off, the valve at the top of the superheater is closed, and a blast of steam is turned into the producer either at the top or the bottom. A moment later a jet of oil is turned into the top of the car-buretor. The heat of the checker-work breaks the oil up into gaseous products which do not readily condense. The oil run takes about six minutes. After the gas leaves the superheater it passes through a water-seal and into the scrubber.

The scrubber is filled with wooden gratings, through which a constant shower of water is falling. The water cools the hot gas and condenses much tar that is formed in the process.

CHAPTER XXXVII

SILICON AND BORON

Silicon (Laboratory Exercise No. 29)

545. Appearance. Like carbon, silicon exists in several different modifications. It is either a brown amorphous powder or a black crystalline substance having a bright metallic lustre.

546. Occurrence. Next to oxygen it is the most abundant element in the earth's crust, forming nearly one-fourth of it by weight. It does not occur in the free condition, but exists in combination with oxygen as silica, SiO_2, which appears as sand and quartz. Silicon dioxide is an acid anhydride and exists in combination with basic oxides, as silicates, which form a large proportion of the common rocks.

547. Physical and chemical properties. Silicon melts at a temperature of about 1400°, and at a higher temperature is converted to a gas. Gaseous silicon burns in air, giving off a white smoke, which is silicon dioxide:

$$Si + O_2 = SiO_2.$$
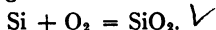
At a high temperature it combines with many elements forming binary compounds, among them being silicon tetrafluoride, SiF_4; silicon tetrachloride, $SiCl_4$; and silicon carbide, SiC.

It dissolves in sodium or potassium hydroxide with the evolution of hydrogen and the formation of potassium silicate:

$$Si + 2 KOH = K_2SiO_2 + H_2.$$
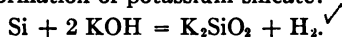
548. Test. In testing for silicon it is usually sufficient to recognize a hard, gritty substance resembling sand, which is insoluble in hydrochloric acid.

In the case of insoluble silicates, however, the substance is first reduced to a fine powder and melted in a platinum crucible with sodium carbonate. This converts the silicon to sodium silicate. The fused mass is dissolved in water and treated with hydrochloric acid. The silicon separates as gelatinous silicic acid:

$$CaSiO_3 + Na_2CO_3 = Na_2SiO_3 + CaCO_3.$$
$$Na_2SiO_3 + 2 HCl = 2 NaCl + H_2SiO_3.$$
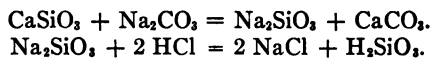
When this is heated the water is driven off and white amorphous silica is left:

$$H_2SiO_3 \text{ heated} = SiO_2 + H_2O.$$
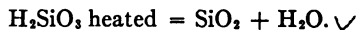
This in turn will completely dissolve in hydrofluoric acid:

$$SiO_2 + 4 HF = SiF_4 + 2 H_2O.$$

366
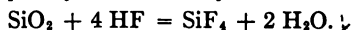
549. Preparation. Silicon may be made by heating sodium or magnesium with sodium silicofluoride, Na_2SiF_6:

$$Na_2SiF_6 + 4\,Na = 6\,NaF + Si.$$
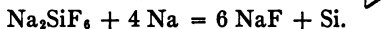
It may also be made by setting fire to a mixture of aluminum powder, sulphur, and sand, and dissolving the cooled mass in hydrochloric acid.

It is obtained as a by-product in the manufacture of silicon carbide (carborundum) in the electric furnace:

$$2\,C + SiO_2 = 2\,CO + Si.$$
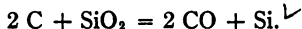
550. Uses. Until recent years silicon was essentially a curiosity and had had no especial use as an element. But since large quantities have been produced, it has found use in the manufacture of iron and steel.

551. Common compounds. Silica, quartz, or rock crystal, SiO_2; sodium or **potassium silicate** (water-glass); silicon tetrafluoride, SiF_4; silicon hydride, SiH_4; hydrofluosilicic acid, H_2SiF_6; **meta-silicic acid,** H_2SiO_3.

552. Silicon fluoride, SiF_4. This is a colorless gas that is always formed when hydrofluoric acid acts upon silica or silicates:

$$SiO_2 + 4\,HF = SiF_4 + 2\,H_2O.$$
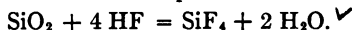
It reacts readily with water to form ortho-silicic acid and **hydrogen silicofluoride,** or **hydrofluosilicic acid:**

$$SiF_4 + 4\,HOH = Si(OH)_4 + 4\,HF.$$
$$4\,HF + 2\,SiF_4 = 2\,H_2SiF_6.$$
$$\overline{3\,SiF_4 + 4\,HOH = Si(OH)_4 + 2\,H_2SiF_6.}$$
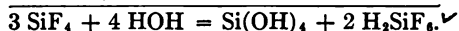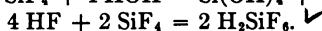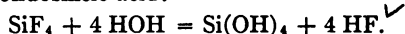
553. Silicon hydride. This compound is a colorless gas that takes fire spontaneously when it comes in contact with the air. It is formed when sodium or magnesium silicide comes in contact with water:

$$Na_4Si + 4\,HOH = 4\,NaOH + SiH_4.$$
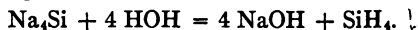
554. Silica, SiO_2. This compound occurs in a great variety of forms. When it is found in large six-sided transparent crystals it is known as **quartz,** or rock crystal. **Amethyst** is quartz,
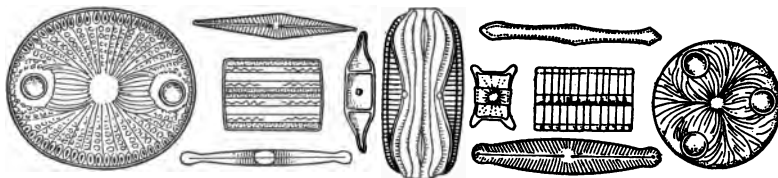
Fig. 116. Diatoms Contained in Infusorial Earth, Magnified 250 Diameters

colored by a trace of manganese. **Agate, jasper,** and **onyx** are amorphous forms of silica. **Infusorial earth** (Fig. 116) is com-

posed of the remains of minute organisms.   Silica forms an important constituent of nearly all vegetable growths.   All sharp grasses, the horsetail, and bamboo contain large quantities.

555. Properties of silica.   Silica is almost insoluble in water and acids.   It can be melted in the oxyhydrogen flame and the electric furnace, and worked into various forms, such as flasks, test-tubes, and crucibles.

Silicon dioxide is an acid anhydride and will unite with the alkalies, forming silicates:

$$SiO_2 + 4\,NaOH = Na_4SiO_4 + 2\,H_2O.$$
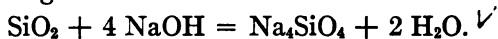
Sodium and potassium silicates are soluble in water and are known as **water-glass.**

When silica is fused with basic oxides it unites with them, forming silicates.   **Glass** is a mixture of various silicates made by melting sand with sodium, potassium, calcium, and lead compounds in varying proportions.

Silica dissolves readily in hydrofluoric acid, forming gaseous silicon tetrafluoride and water.

When fused with sodium or potassium carbonate carbon dioxide is liberated and the corresponding silicate is formed:

$$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2.$$
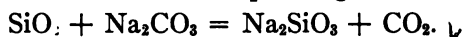
556. The silicic acids.   If water-glass solution be treated with a small amount of hydrochloric acid, the whole solution is soon transformed to a jelly.   This jelly consists of silica combined with an uncertain amount of water and may be considered as containing **ortho-silicic acid,** H_4SiO_4:

$$Na_4SiO_4 + 4\,HCl = H_4SiO_4 + 4\,NaCl.$$
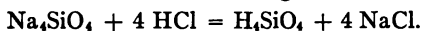
If this jelly be washed thoroughly by straining through cloth, with frequent rinsings to remove the sodium chloride, and the product dried in the air, a white amorphous powder is obtained, which is **meta-silicic acid,** H_2SiO_3.   And if the dry powder be heated, the last molecule of water is driven off and amorphous silica is obtained:

$$H_2SiO_3 \text{ heated} = SiO_2 + H_2O.$$
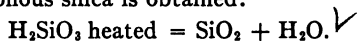
Many of the natural silicates are very complex compounds, and may be considered as salts of the polysilicic acids.   A **polysilicic acid** may be considered as derived from two or more molecules of orthosilicic acid minus one or more molecules of water:

$$2\,H_4SiO_4 - H_2O = H_6Si_2O_7.$$
$$2\,H_4SiO_4 - 3\,H_2O = H_2Si_2O_5.$$
$$3\,H_4SiO_4 - 4\,H_2O = H_4Si_3O_8.$$
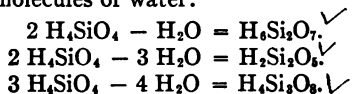
The silicic acids are extremely weak; that is, they are very slightly dissociated in solution, furnishing a very small quantity of hydrogen ions.

Boron

557. Appearance. Boron is usually an amorphous black powder, but may be obtained in the crystalline form by allowing a solution of it in molten aluminum to slowly cool. The aluminum may be dissolved in hydrochloric acid, leaving the crystals of boron.

Occurrence. It does not occur in the free condition, but chiefly as boric acid, H_3BO_3, in Tuscany; sodium tetraborate, $Na_2B_4O_7$, or borax and colemanite, $Ca_2B_6O_{11} + 5 H_2O$, in California and Nevada.

558. Properties. The crystallized element is not unlike diamond in hardness and lustre. Chemically it resembles silicon. It burns when heated sufficiently in oxygen, forming boron trioxide, B_2O_3, the anhydride of boric acid. It unites directly with fluorine and chlorine and dissolves in the caustic alkalies, forming borates and hydrogen:

$$2 B + 6 KOH = 2 K_3BO_3 + 3 H_2.$$
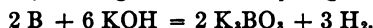
559. Test for boric acid and borates. It is frequently desirable to test various food products for the presence of boric acid or borates. About 25 g. of the sample should be made distinctly alkaline with lime-water and dried on the steam bath. The dry material is then burned to an ash in a crucible over the flame or in a muffle. The ash is acidified with hydrochloric acid and boiled with 10 or 15 c.c. of water and filtered. A piece of turmeric-paper moistened in the liquid and dried will turn red, if either free or combined boric acid is present. The red color will be turned to olive-green when moistened with ammonium hydroxide.

560. Preparation. Boron may be prepared by the reduction of boron trioxide by heating with magnesium powder:

$$B_2O_3 + 3 Mg = 2 B + 3 MgO.$$
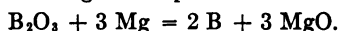
Uses. Boron in the elementary state has no especial use. The oxide is used in the manufacture of glass. Boric acid is used as an antiseptic and food preservative. Borax is used as a washing-powder, as a flux in soldering metals, and as a food preservative.

561. Compounds. Boron oxide, B_2O_3; orthoboric acid, H_3BO_3; sodium tetraborate, or borax, $Na_2B_4O_7 + 10 H_2O$.

Boron oxide, B_2O_3. Boron oxide is a brittle, glassy solid that dissolves in water readily, forming boric acid. It is readily made by heating orthoboric acid:

$$2 H_3BO_3 = B_2O_3 + 3 H_2O.$$

562. Orthoboric acid, H_3BO_3. Orthoboric acid occurs in the form of brilliant, colorless scales. It is slightly soluble in cold water and readily soluble in hot. Its solution has a slight acid reaction and is slightly volatile with steam. It is readily prepared by treating a hot saturated solution of borax with a slight excess of hydrochloric acid. On cooling,

the boric acid crystallizes and may be filtered off. A solution of this acid is much used in eye-lotions.

563. Metaboric acid. If orthoboric acid be heated carefully, 1 molecule of water will separate, leaving metaboric acid, HBO_2:

$$H_3BO_3 = HBO_2 + H_2O.$$

564. Tetraboric acid. If 4 molecules of metaboric acid be heated, 1 molecule of water evaporates, leaving tetraboric acid. The sodium salt of this acid, with 10 molecules of water, constitutes **ordinary crystallized borax:**

$$4\,HBO_2 = H_2B_4O_7 + H_2O.$$

565. Borax, or sodium tetraborate, $Na_2B_4O_7 + 10\ H_2O$. Borax is found in the free condition in India and California. It dissolves in water and may be caused to crystallize therefrom with either 5 or 10 molecules of water of crystallization.

Since it is a salt of a very weak acid with a strong base, it is hydrolyzed in water solution with the formation of some free sodium hydroxide. For this reason it is valuable as a washing-powder:

$$Na_2B_4O_7 + 7\,H_2O \rightleftharpoons 4\,H_3BO_3 + Na^+ + Na^+ + OH^- + OH^-.$$
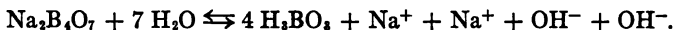
When heated it swells, on account of the escape of the water, and finally melts to a clear glass-like body known as **borax glass.**

Melted borax glass dissolves basic oxides readily. It is therefore used as a flux in soldering metals together. If it were not for the flux, oxides of the metals would form and the solder would not unite with the metal. This ability to unite with basic oxides is readily understood when it is considered that the molecule of borax contains 1 molecule of boron oxide that is free to combine. That is, we may consider that the substance has the formula $2\,NaBO_2 \cdot B_2O_3$. Traces of certain metallic oxides give borax glass characteristic colors. Copper, in the form of cupric oxide, colors the glass green, manganese pink, and cobalt blue. This fact is often made use of in testing for the presence of these elements in the course of qualitative analysis.

CHAPTER XXXVIII

Glass, Pottery, and Cement

Glass

566. Glass. Glass is an amorphous mixture of the silicates of sodium or potassium and calcium or lead. It always contains one of the alkali silicates and either the silicate of calcium or lead. It is possible that it should contain both sodium or potassium and also both calcium and lead. A glass might be a soda-lime or a soda-lead glass. Potassium oxide might take the place of the soda.

567. Composition. While the exact composition of glass is uncertain, still the composition of a soda-lime glass is very close to the theoretical composition called for by the formula $Na_2O \cdot CaO(SiO_2)_6$. This could be considered as a mixture of two silicates, $Na_2Si_2O_7$ and $CaSi_2O_7$.

568. Color. The color of glass is produced by introducing various metallic oxides which give colored silicates in place of some of the calcium or lead. Ferric oxide colors glass brown, cupric oxide green, cobalt oxide blue.

569. Materials. Silica is usually furnished in the form of very clean sand free from iron. The alkali oxide is furnished by either sodium carbonate or sodium sulphate. Lead is used in the form of lead oxide, PbO; litharge, or red lead, Pb_3O_4. Lime is used in the form of pure marble dust or limestone.

570. Melting the ingredients. The pots used for melting glass are made of clay and are either open or closed (Fig. 117). They are commonly arranged in a circular furnace which is fired from the centre (Fig. 118). There are openings in the side opposite each pot to enable the glass-blower to collect the partly molten glass on his blowpipe. The materials are first heated very hot. This renders the liquid glass very thin and allows all of the bubbles of gas to escape.

Fig. 117

After standing for a time the undissolved materials are skimmed off and the glass allowed to cool to a consistency required for blowing.

571. Reactions. The reactions taking place during the melting are approximately as follows:

$$Na_2CO_3 + 3 SiO_2 = Na_2Si_3O_7 + CO_2.$$
$$CaCO_3 + 3 SiO_2 = CaSi_3O_7 + CO_2.$$
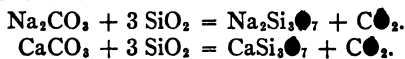
If a sulphate is used, enough carbon is introduced to reduce it to a sulphite:

$$Na_2SO_4 + C = Na_2SO_3 + CO.$$
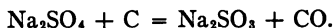
The sulphite then reacts with the silica, and sulphur dioxide is set free:

$$Na_2SO_3 + 3 SiO_2 = Na_2Si_3O_7 + SO_2.$$
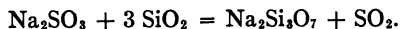
572. Potash-lime glass. This is a hard glass that resists chemicals well and is largely used in the manufacture of chemical glassware.

A
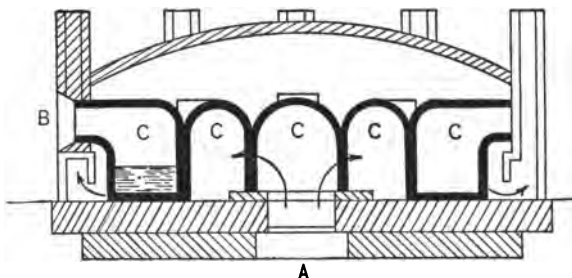
FIG. 118

573. Soda-lime glass. This is harder than the potash-lime glass, but more easily fusible. It is used for plate glass, ordinary window-glass, and sky-light-glass.

574. Potash-lead glass. A glass made from potassium oxide, lead oxide, and silica is called **flint glass.** It is very easily fusible, easy to cut, and has a high refractive power. Flint glass is used for optical instruments, for cut glassware, and special modifications of it for making imitation diamonds.

Pottery, China, and Porcelain

575. Materials. The important material from which all varieties of pottery-ware are made is clay. **Clay** is a hydrated aluminum silicate formed by the decomposition of feldspar or feldspathic rocks, mixed with silica and a varying amount of other impurities.

Feldspar has the composition shown by the formula $K_2O \cdot Al_2O_3 \cdot 6 SiO_2$.

By the action of water and carbon dioxide through thousands of years, the potassium oxide has been changed to potassium carbonate and washed away, leaving a hydrated aluminum silicate known as **clay,** having the composition $Al_2O_3 \cdot 2 SiO_2 \cdot 2 H_2O$, mixed with some silica.

Kaoline, or china clay. When the clay has been formed by the decomposition of pure feldspar and is found in its original position, it is a pure-white light powder containing almost no impurity but silica, and is called kaoline.

Ordinary clay contains many impurities gained in being washed from its original place of formation to the place of deposit. The blue color of some clay is due to the presence of iron in the ferrous condition, which in the course of baking is converted to the ferric, giving the finished material a brick-red color.

576. Manufacture. After the clay has been mixed with other materials to give the finished product the required properties, the potter fashions it into the various shapes. These are carefully dried and then fired in a kiln. The first firing hardens them to a stone-like condition, but they are rough on the surface and perhaps porous.

577. Glazing. Articles to be glazed are dipped into the pulverized glazing material suspended in water. Enough of the material adheres to the object to furnish a smooth glass-like coating when it is reheated (Fig. 119). It is important that the glaze should have the same coefficient of expansion as the body itself; otherwise it will soon be filled with minute cracks.

Jugs, crocks, drain-pipes, and coarse earthenware are glazed by throwing salt into the fire, when the first baking is nearly complete. The salt is vaporized, and the sodium forms a fusible silicate on the surface of the objects.
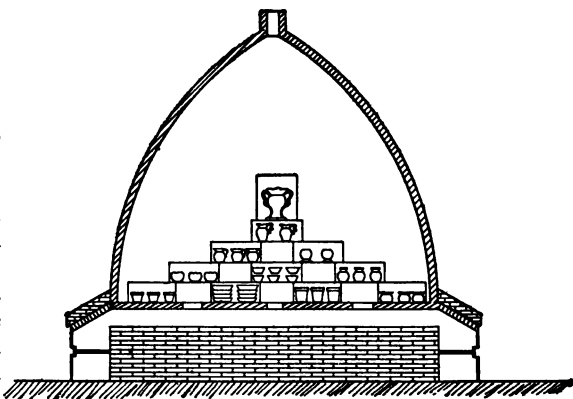
578. Porcelain. The Royal Berlin porcelain of the laboratory is made of kaoline, quartz, and feldspar in definite proportions. At the first baking the materials melt together, forming a non-porous body which is afterward glazed with pure feldspar. This ware is almost infusible and is hardly attacked by ordinary chemicals.

579. China. By china is not meant the ordinary crockery of the household, but a particular variety of porcelain made from kaoline mixed with bone ash and glazed with a lead-boric-acid glass.

Cement and Concrete

580. Cement. Cement differs from lime and mortar in that it does not require carbon dioxide for setting and will become hard under water. It consists of a mixture of certain silicates of calcium mixed with calcium

aluminate. There are three different classes of cement which differ chiefly in the mode of manufacture.

Kinds of cement. **Puzzolan** is a cement made by grinding volcanic ash and mixing it with the additional amount of lime necessary. **Natural cement** is made by burning an argillaceous (containing clay) limestone sufficiently to drive off all of the carbon dioxide, but not enough to vitrify it, and adding just water enough to slake the lime. **Portland cement** is purely an artificial product made by mixing, burning, and pulverizing the materials in the proper proportion. This cement is by far the most important of the three. The production in the United States alone in 1907 was about 50,000,000 barrels.

581. Manufacture. The process consists:

1. In mixing about 75 parts of calcium carbonate with about 20 parts of clay rich in silica.

2. This mixture is very finely ground and intimately mixed.

3. This finely ground material is sent through a rotary kiln (Fig. 120) about 100 ft. long, where it is heated to a high temperature, but not sufficiently to vitrify it. The product of this heating is called **clinker.**
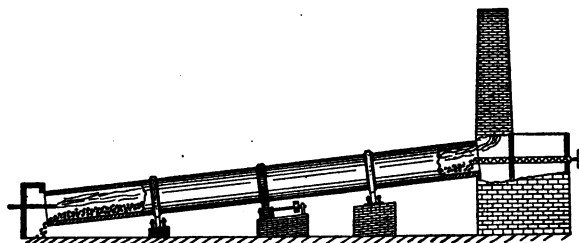
FIG. 120

4. The clinker is so finely ground that most of it will pass through a 200-mesh sieve—that is, a sieve containing 40,000 holes to the square inch.

582. Composition and setting. Good Portland cement is supposed to contain the compounds whose composition corresponds to the formulas Ca_3SiO_5, Ca_2SiO_4, and $Ca_3Al_2O_5$. When mixed with water the calcium silicates are hydrolyzed, forming calcium metasilicate and calcium hydroxide. It is possible that in time the calcium hydroxide unites with the calcium aluminate.

Analysis of a Portland cement mixture ready for burning:

Silica (SiO_2)..12.85%
Aluminum oxide (Al_2O_3).............................. 4.92%
Ferric oxide (Fe_2O_3)................................. 1.21%
Calcium carbonate ($CaCO_3$)..........................76.36%
Magnesium carbonate ($MgCO_3$)...................... 2.13%

583. Concrete. Concrete is a mixture of cement, sand, and broken stone in varying proportions. 1 part of cement to 3 of sand, and 5 of

broken stone or gravel, with enough water to render the mixture semifluid, makes a satisfactory mixture. It "sets" in a few hours and if kept moist it soon becomes as hard as stone.

584. Uses. Concrete is rapidly replacing stone for foundations of all kinds. Iron railroad bridges are being replaced by massive concrete arches, and whole buildings are constructed of this material.

CHAPTER XXXIX

The Metals

All of the elements may be divided into two distinct classes, metals and non-metals. Of the 80 elements only about 20 are non-metals, the rest being metals. There are a few elements on the line between metals and non-metals which have some properties of both.

585. Properties of metals. All metals, in thin section, are opaque, are good conductors of electricity, and have a metallic lustre. They also furnish positively charged ions, and their oxides are usually basic.

Properties of non-metals. All non-metals, in thin section, are transparent, are poor conductors of the electric current, and have no metallic lustre. They furnish negatively charged ions in solution and their oxides are always acidic.

586. Alloys. Alloys are mixtures of two or more metals. Brass is a mixture of copper and zinc. Other alloys will be considered under the head of the chief metal involved.

Metallurgy is the art of extracting metals from their ores. It also includes the art of separating metals from the impurities and of mixing metals to form alloys.

587. Ores. An ore is the natural material from which a pure metal may be extracted. The ore contains either the free metal or its oxide, sulphide, carbonate, or other salt mixed with rock and earthy material. Although an element be found virtually in the free condition, it is never absolutely pure.

588. Preliminary treatment of the ore. Immediately after being mined, the ore is picked over by hand, if necessary, to separate the valuable part from the worthless rock. After pulverizing, the ore goes through some kind of a concentrating process, usually involving the use of water, in which the heavier ore-bearing particles are separated from the lighter earthy material.

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589. Roasting. Many ores containing the metal in the form of sulphides, arsenides, or carbonates must be heated in an oxidizing atmosphere in order to convert the metal to the oxide. Such a process is called "roasting." The roasting may be carried out in several ways. If the ore is rich in sulphur, it is possible to set it on fire in the open air with the help of a little fuel, and the burning goes on for weeks at a time, the sulphur passing off as sulphur dioxide.
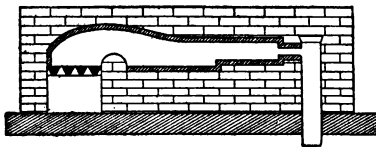
FIG. 121

Or the ore may be roasted in a variety of **reverberatory furnace,** in which it is constantly turned over and over in a shallow layer in an oxidizing atmosphere.

590. Reduction. In order to obtain the metal from the oxide, it is necessary to heat the oxide with a reducing agent. This may be accomplished either in a reverberatory furnace in which it comes in contact with the reducing flame of a coal or gas fire, or in some variety of a blast-furnace.

In the reverberatory furnace the roasted ore is placed on the hearth and is heated in a reducing flame from either coal or gas (Fig. 121). The chief reducing agent here is carbon monoxide.

In the blast-furnace the ore with fuel and lime is fed in at the top, and a blast of air is blown in at the bottom. The fuel, burning to carbon monoxide, produces the reducing atmosphere necessary for converting the oxide to the metal.

CHAPTER XL

TIN AND LEAD

Tin (Laboratory Exercise No. 30)

591. Appearance and occurrence. Tin is a silver-white metal. It does not occur in the free condition, but chiefly as stannic oxide, SnO_2, also called **tinstone,** or **cassiterite,** in Wales and the East Indies.

592. Physical properties. Tin is not very ductile, but may be beaten out into very thin sheets forming tin-foil.

It melts at 244°, boils at 1525°, and has a specific gravity of 7.3. It is decidedly crystalline, and if a piece of tin be treated with hydrochloric acid the surface shows a peculiar frost-like structure. A bar of tin when bent gives out a creaking sound called "tin cry." This is probably caused by the crystals rubbing together.

593. Chemical properties. Tin does not oxidize in the air, but when heated it burns, forming an intense white light, and gives off a white smoke, SnO_2.

It forms two classes of compounds: **stannous,** in which it has a valence of 2; and **stannic,** in which it has a valence of 4.

It dissolves in hydrochloric acid with the formation of stannous chloride and the evolution of hydrogen:

$$Sn + 2\,HCl = SnCl_2 + H_2.$$
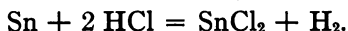
Stannous chloride solution treated with an oxidizing agent in the presence of hydrochloric acid is converted to stannic chloride, $SnCl_4$:

$$SnCl_2 + Cl_2 = SnCl_4.$$

Hydrogen sulphide passed through a solution of stannous chloride produces a brown precipitate of **stannous sulphide,** SnS; and through a solution of stannic chloride a yellow precipitate of **stannic sulphide,** SnS_2.

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Stannous sulphide dissolves in a solution of yellow ammonium sulphide with the formation of soluble **ammonium thiostannate:**

$$SnS + S + (NH_4)_2S = (NH_4)_2SnS_3.$$
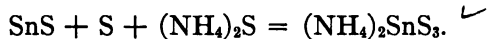
If this solution be treated with hydrochloric acid, stannic sulphide and sulphur are precipitated and hydrogen sulphide is set free:

$$(NH_4)_2SnS_3 + 2\ HCl = 2\ NH_4Cl + SnS_2 + H_2S.$$
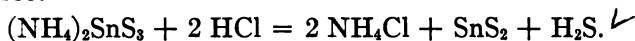
Stannous chloride is oxidized in solution by mercuric chloride to stannic chloride with the precipitation of mercury:

$$SnCl_2 + HgCl_2 = SnCl_4 + Hg.$$
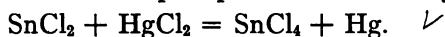
When tin is boiled with nitric acid it is converted to an amorphous white powder called **metastannic acid:**

$$4\ HNO_3 = 2\ H_2O + 4\ NO_2 + 2\ O.$$
$$2\ O + Sn = SnO_2.$$
$$\underline{SnO_2 + H_2O = H_2SnO_3.}$$
$$4\ HNO_3 + Sn = H_2SnO_3 + 4\ NO_2 + H_2O.$$
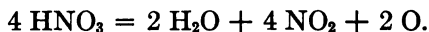
594. Test. The finely divided metal dissolves in hydrochloric acid, from which it is precipitated as brown stannous sulphide by hydrogen sulphide.

It is also converted to a white amorphous powder when boiled with strong nitric acid.

595. Preparation. (1) A piece of zinc suspended in a solution of stannous chloride rapidly precipitates the tin in the form of long, leaf-like crystals, an equivalent amount of zinc going into solution as the chloride:

$$SnCl_2 + Zn = ZnCl_2 + Sn.$$
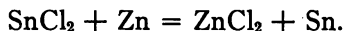
Electrolytic solution pressure. All metals when immersed in a liquid have a tendency to send ions into solution. This tendency is called the electrolytic solution pressure. For some metals, like sodium, magnesium, and zinc, it is very high, and for others, like copper, silver and gold, it is very low.

In the above case the zinc has a very high solution tension, and proceeds to send zinc ions into solution. Each ion, carrying a positive charge of electricity, leaves a corresponding amount of negative electricity on the zinc. The tin ions in

the solution drift to the zinc, where they give up their positive charges and are set free as metallic tin.

(2) Tin oxide is easily reduced on a piece of charcoal by means of the reducing flame of a blowpipe:

$$SnO_2 + 2\ CO = 2\ CO_2 + Sn.$$
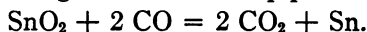
(3) **Reduction from the ore.** Tinstone, SnO_2, is heated with charcoal in a reverberatory furnace, producing impure tin.

The impure tin is melted on a slightly inclined hearth. The pure tin runs down the incline, and the impurities remain behind.

596. Uses. (1) For covering thin sheet iron, producing what is called **sheet tin.** This is the tin from which all ordinary tinware is made.

(2) For making alloys. **Solder,** such as used by tinsmiths, contains equal weights of tin and lead. **Bronze** is an alloy of copper and tin. **Gun metal** contains about 90 per cent copper and 10 per cent tin.

(3) An alloy of tin and mercury called **tin amalgam** was formerly used for silvering mirrors.

597. Compounds. Stannic oxide, or tinstone, SnO_2; stannic chloride, $SnCl_4$; stannic sulphide, SnS_2; metastannic acid, H_2SnO_3; ammonium thiostannate $(NH_4)_2SnS_3$; **stannous chloride,** $SnCl_2$; **stannous sulphide,** SnS.

Lead (Laboratory Exercise No. 30)

598. Appearance. Lead when freshly cut shows a brilliant bluish-white metallic surface. In air containing the least moisture the clean surface soon turns to a dull-gray color.

599. Occurrence. The chief source of lead is **galena,** PbS, a heavy lead-colored mineral that crystallizes in cubes.

600. Physical and chemical properties. Lead is an extremely soft metal. It melts at 334° and boils at 1500°. Its specific gravity is 11.25. Under ordinary conditions lead does not burn. When very finely divided, however, it takes fire spontaneously. It has valences of 2 and 4. The oxide corresponding to a valence of 2 is PbO, lead oxide, also known as **litharge.** It is basic toward acids, but will dissolve in sodium hydroxide, forming **sodium plumbite:**

$$2\ NaOH + PbO = Na_2PbO_2 + H_2O.$$
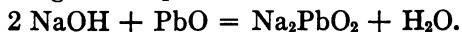
Red lead, Pb_3O_4, might be considered a compound of lead dioxide, PbO_2, with 2 molecules of PbO. When this compound is treated with nitric acid the basic oxide, PbO, is converted to the nitrate and the insoluble brown dioxide, PbO_2, is left:

$$Pb_3O_4 + 4 HNO_3 = 2 Pb(NO_3)_2 + PbO_2 + 2 H_2O.$$
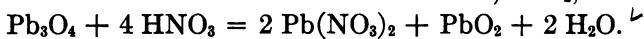
601. Action of acids. Lead is virtually insoluble in sulphuric, hydrochloric, and acetic acids.

Hot dilute nitric acid dissolves lead easily, with the formation of lead nitrate and nitric oxide:

$$2 HNO_3 = H_2O + 2 NO + 3 O.$$
$$3 O + 3 Pb = 3 PbO.$$
$$\underline{3 PbO + 6 HNO_3 = 3 Pb(NO_3)_2 + 3 H_2O.}$$
$$3 Pb + 8 HNO_3 = 3 Pb(NO_3)_2 + 4 H_2O + 2 NO.$$
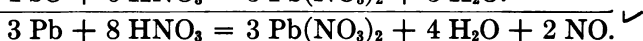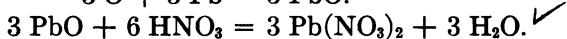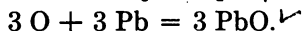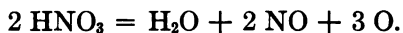
602. Action of water on lead. Pure distilled water containing no air or carbon dioxide has no effect on lead. But distilled water in contact with air, as well as rain-water, dissolves it quite readily, forming lead hydroxide.

Spring-water, or hard water in general, has little effect, for the reason that the lead soon becomes covered with a protecting coating of carbonate which prevents much further action.

Since the drinking water of the average house passes through lead pipes, it would be well never to use water that has been standing in the pipes.

603. Tests. A solution of a lead salt treated with a soluble chloride gives a white precipitate of lead chloride:

$$Pb(NO_3)_2 + 2 NaCl = \underline{PbCl_2} + 2 NaNO_3;$$
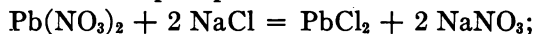
with a soluble sulphate gives a white precipitate of lead sulphate:

$$Pb(NO_3)_2 + H_2SO_4 = \underline{PbSO_4} + 2 HNO_3;$$
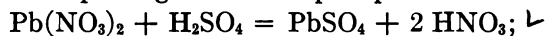
with potassium chromate or dichromate gives a yellow precipitate of lead chromate:

$$Pb(NO_3)_2 + K_2CrO_4 = \underline{PbCrO_4} + 2 KNO_3;$$
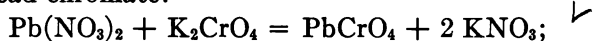
and with hydrogen sulphide gives a black precipitate of lead sulphide:

$$Pb(NO_3)_2 + H_2S = \underline{PbS} + 2 HNO_3.$$
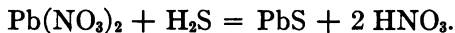
The preceding reactions serve very well for testing for lead in a soluble compound. If the substance is a metal, it should be dissolved in nitric acid and the solution evaporated with a

few drops of sulphuric acid.   Any lead will be converted to the sulphate, which will appear as an insoluble white residue on the addition of water.

604. Preparation.   Reduction by hydrogen.   Any oxide of lead heated in a tube through which a stream of hydrogen or illuminating gas is passing is readily reduced to the metal:

$$Pb_3O_4 + 4 H_2 = 3 Pb + 4 H_2O.$$
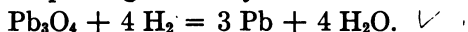
605. Reduction by charcoal.   An oxide of lead heated on a piece of charcoal in the reducing flame of the blowpipe is at once reduced to lead:

$$PbO + CO = Pb + CO_2.$$
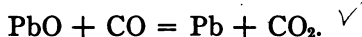
606. Electrolytic method.   A solution of a lead salt is converted to lead and the corresponding acid when an electric current is passed through it.

$Pb(NO_3)_2$ gives in solution the ions Pb^{++} and $NO_3^- + NO_3^-$. The positive ions of lead drift toward the negative electrode, where they give up their positive charges and are set free as metallic lead.   The negative ions NO_3^- drift toward the positive electrode, where they give up their negative charges and react with the water to form oxygen and nitric acid:
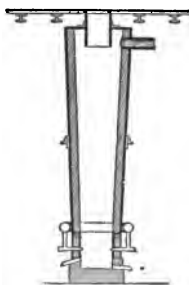
$$4 NO_3 + 2 H_2O = 4 HNO_3 + O_2.$$
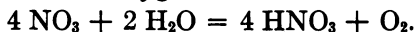
607. Reduction from the ore.   Lead ores are usually roasted before going to the reducing furnace.   In this roasting some of the sulphide is changed to the oxide, and sulphur dioxide is set free:

$$2 PbS + 3 O_2 = 2 PbO + 2 SO_2.$$
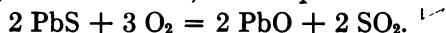
Also some of the sulphide is converted to the sulphate:

$$PbS + 2 O_2 = PbSO_4.$$
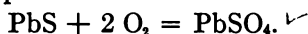
The actual reduction is brought about either in a reverberatory furnace or a blast-furnace (Fig. 122).   In either case the chief reactions are as follows:

$$PbO + C = Pb + CO.$$
$$PbO + CO = Pb + CO_2.$$
$$PbS + 2 PbO = 3 Pb + SO_2.$$
$$PbSO_4 + PbS = 2 Pb + 2 SO_2.$$
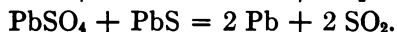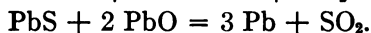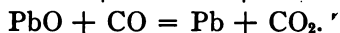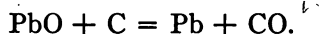
608. Precipitation from solution. If a piece of zinc be suspended in a solution of a lead salt, crystalline lead soon collects about the zinc in long, thin leaves. The amount of lead precipitated is the exact chemical equivalent to the amount of zinc that goes into solution:

$$Pb(C_2H_3O_2)_2 + Zn = Pb + Zn(C_2H_3O_2)_2.$$
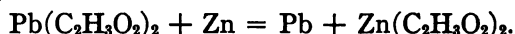
This reaction is similar to the precipitation of tin by zinc. The solution pressure of the zinc being greater than that of the lead, the zinc sends its ions into the solution, and the lead ions drift to the piece of zinc, where they give up their positive charges and are set free as metallic lead.

609. Uses. Lead is very slightly acted upon by many acids and salt solutions; it is therefore extensively used for lining all kinds of iron vessels used in the chemical industries. Chambers for the manufacture of sulphuric acid are entirely constructed of heavy sheet lead.

It is also used for making lead pipe and for covering electric cables. Large quantities of lead are used in the manufacture of shot. For this purpose the melted lead is alloyed with a small quantity of arsenic and allowed to fall in different-sized drops through a high tower into water. In falling the lead takes the spherical form and solidifies before reaching the bottom.

Much lead is converted into lead compounds, especially lead oxide and white lead used in the paint industry.

610. Alloys. Lead is alloyed in a great many different proportions with other metals, especially tin, bismuth, antimony, cadmium, and copper. These alloys go under many different names and are used for a great variety of purposes. The following table gives the approximate compositions of some common alloys:

Name	Lead	Tin	Antimony	Bismuth
Tin solder........	50	50	....	....
Pewter	20	80	....	....
Rose's alloy......	25	25	....	50
Bearing-metal.....	75	2	23	....
Stereotype metal...	20	30	....	50

611. Common compounds. Lead monoxide, or **litharge,** PbO; **lead dioxide,** PbO_2; **red lead,** Pb_3O_4; **lead nitrate,** $Pb(NO_3)_2$; lead sulphide, PbS; lead sulphate, $PbSO_4$; lead acetate, $Pb(C_2H_3O_2)_2$; basic lead carbonate, or **white lead,** $2 PbCO_3 \cdot Pb(OH)_2$; lead chromate, or ,chrome yellow, $PbCrO_4$.

612. The oxides of lead. Lead monoxide may be made by heating lead in an oxidizing atmosphere. It is a yellow solid and in the powdered form is known as **litharge.** It may also be made by heating the nitrate or carbonate. It is basic and dissolves in all acids, forming the corresponding lead salts. Toward sodium and potassium hydroxides in solution it acts acidic, uniting with them to form plumbites:

$$PbO + 2 NaOH = Na_2PbO_2 + H_2O.$$
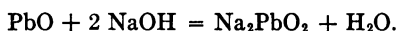
613. Red lead, or **minium,** Pb_3O_4, is a compound of 2 molecules of the monoxide with 1 molecule of the dioxide. It can be formed by heating the monoxide in oxygen at about 600°. It may be considered as the salt formed by lead monoxide with orthoplumbic acid:

$$2 PbO + H_4PbO_4 = Pb_2PbO_4 + 2 H_2O, \text{ or}$$
$$2 PbO + PbO_2 = Pb_2PbO_4.$$
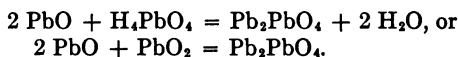
When heated it gives up oxygen and is converted to the monoxide:

$$2 Pb_3O_4 = 6 PbO + O_2.$$

614. Lead dioxide, PbO_2. This is a brown powder formed by the action of nitric acid on red lead. Since red lead may be considered as a compound of lead monoxide with lead dioxide, when it is treated with the acid the monoxide is converted to lead nitrate and the dioxide is left as an insoluble residue:

$$Pb_2PbO_4 + 4 HNO_3 = 2 Pb(NO_3)_2 + PbO_2 + 2 H_2O.$$
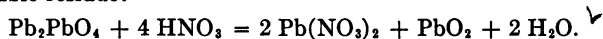
Lead dioxide will liberate chlorine from hydrochloric acid with the formation of lead chloride:

$$PbO_2 + 4 HCl = PbCl_2 + 2 H_2O + Cl_2.$$
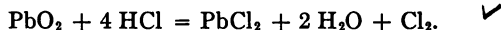
It is used in the manufacture of the lead plates for storage-batteries.

615. Lead acetate, or sugar of lead, $Pb(C_2H_3O_2)_2 \cdot 3 H_2O$. This compound is made by the action of acetic acid on lead monoxide. If an excess of the oxide is used, a basic salt is obtained. Its solution has a slightly sweet taste, from which fact the name "sugar of lead" is derived.

616. Lead carbonate, $PbCO_3$. If a solution of a lead salt be treated with a solution of bicarbonate of soda, a precipitate of normal lead carbonate is formed; but if it is treated with a solution of sodium carbonate, a precipitate of basic lead carbonate is obtained. The formula of this salt is $2 PbCO_3 \cdot Pb(OH)_2$. This compound is essentially the same as the material known as white lead used in paint.

The Manufacture of White Lead

617. White lead is of great importance on account of its use in the manufacture of paint. It is manufactured by several well-known processes at present, only one of which, the old **Dutch process,** will be described.

618. The old Dutch process. The lead is first cast in the form of flat perforated plates, known as **buckles,** weighing about 1 lb. each (Fig. 123). Sixteen of these buckles are placed in an earthenware pot of a peculiar shape (Fig. 124), in the lower glazed portion of which is placed a pint of 3-per-cent acetic acid. The loaded pots are then built up into a stack containing ten or twelve layers, as shown in Fig. 125.
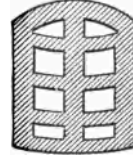
Fig. 123

Each layer of the pots is covered with boards, and these in turn with a thick layer of a mixture of tan-bark and manure. The whole stack is enclosed and allowed to stand for about one hundred and twenty days.

During this time corrosion of the lead takes place. It is probable that in the moist atmosphere of the stack lead hydroxide is first formed.
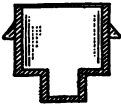
Fig. 124

This, in the presence of the fumes of acetic acid, is changed to lead acetate, which is acted upon by the excess of carbon dioxide from the fermentation of the tan-bark and manure and converted to a basic carbonate.

At the end of the time the stack is pulled down and the remnants of the buckles, covered with crude white lead, are sent through rollers which separate the white product from the remaining lead. White lead is sold in the paint stores either in the form of a finely divided, dry white powder or a paste made by grinding the dry powder in linseed-oil. The paste is readily thinned with oil or turpentine and, after the addition of a little liquid known as a "drier," is ready for use as paint.

Paint

619. Paint consists of a finely divided opaque solid called the **body,** intimately mixed with and suspended in a liquid called the **vehicle,** together with a small proportion of a Japan varnish known as a **drier.** The body of

Fig. 125

the paint should be a good quality of white lead. The vehicle should be either raw or boiled linseed-oil or turpentine, and the drier a ma-

terial made by dissolving manganese dioxide or lead oxide in either linseed-oil or rosin and diluting with turpentine. It is important that the oil used should be what is known as a drying-oil; that is, one that will become hard in time on exposure to the air. Colored paints are produced by substituting for part of the body varying proportions of highly colored pigments or mixtures of pigments to produce the required color.
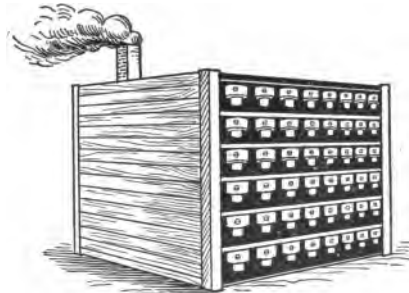
620. Adulterations and substitutes. Ready-mixed paints are seldom of the white-lead, linseed-oil variety. In place of white lead or mixed with it are used pulverized barium sulphate, known as **barytes,** and precipitated calcium carbonate, known as **whiting.** Neither of these materials is as efficient as white lead, for the reason that the particles are transparent and therefore the paint has not the same "covering power." In place of linseed-oil as the vehicle, or mixed with it, are found corn-oil, cotton-seed-oil, fish-oil, and mineral oil.

621. Lead chromate, or **chrome yellow,** $PbCrO_4$. This substance is a bright-yellow insoluble powder formed as a precipitate when a soluble chromate or dichromate is added to a solution of a lead salt. It is the basis of many yellow paints and, mixed with a blue pigment, is a constituent of some green paints:

$$K_2CrO_4 + Pb(NO_3)_2 = \underline{PbCrO_4} + 2\ KNO_3.$$
$$K_2Cr_2O_7 + H_2O + 2\ Pb(C_2H_3O_2)_2 = \underline{2\ PbCrO_4} + 2\ KC_2H_3O_2 +$$
$$2\ HC_2H_3O_2.$$
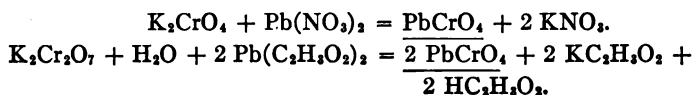
CHAPTER XLI

The Alkali Metals

Sodium, Potassium, Ammonium

Sodium (Laboratory Exercise No. 31)

622. Appearance and occurrence. Sodium is a soft silver-white metal. It does not occur in the free condition, but does occur very widely distributed in the form of compounds. Common salt, or sodium chloride, NaCl, is by far the commonest compound. This substance forms about two-thirds of all of the solid matter dissolved in the sea-water, and is also found as rock salt in New York State, Michigan, West Virginia, and Louisiana. It is also found in the form of sodium nitrate, or Chili saltpetre, in South America, and in certain varieties of feldspar.

623. Physical properties. Its most characteristic property is its softness. It is easily cut with a knife, and with a suitable hand-press it may be forced out through a small hole in the form of wire. It has a specific gravity of about .97, which results in its floating on water. It melts at 95.6° and boils at 742°. Sodium and all sodium compounds color the Bunsen flame bright-yellow.

624. Chemical properties. Perfectly clean, bright, silver-white sodium remains unchanged in dry air or in a dry, inactive gas such as nitrogen or hydrogen. In the presence of a small quantity of water vapor, however, it rapidly tarnishes; and, if a large surface in the form of thin slices be exposed, it will melt and may even take fire.

This tarnishing is due largely to the formation of sodium hydroxide:

$$2\,Na + 2\,HOH = 2\,NaOH + H_2.$$
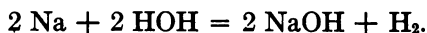
The metal may be melted without taking fire; but, if heated

very hot, it will burst into a bright-yellow flame with the formation of two oxides, Na_2O and Na_2O_2.

When a small piece is placed on cold water, it immediately melts and runs about, generating hydrogen and sodium hydroxide, which goes into solution. When the action is over, a small liquid globule of sodium hydroxide remains for a moment floating on the surface. It is dangerous to throw a large piece of the metal on water, for the hydrogen, instead of escaping, unites with the melted metal forming **sodium hydride,** causing the globule to increase in size instead of decreasing, and the compound soon explodes with violence, throwing pieces of burning sodium about. The experiment of collecting hydrogen from the decomposition of water by sodium held under a receiver in a so-called sodium spoon should also be carefully avoided, as it frequently results in dangerous explosions.

On account of its great attraction for oxygen, sodium is a powerful reducing agent, and will extract the oxygen from nearly all of the oxides when heated with them. Sand heated with the metal readily gives up its oxygen, forming sodium oxide and silicon:

$$SiO_2 + 4\,Na = 2\,Na_2O + Si.$$
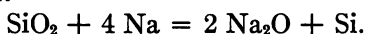
The burning metal will continue to burn when thrust into carbon dioxide and some specks of carbon may be seen.

Sodium alloys with many other metals, especially with mercury, with which it forms a crystalline compound known as **sodium amalgam.**

The metal unites directly with the halogens, forming the corresponding halogen salts:

$$2\,Na + Cl_2 = 2\,NaCl.$$
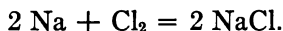
625. Test. Sodium is most readily recognized by the yellow color it and its compounds impart to the Bunsen flame.

626. Preparation. Sodium may be made in minute quantities in the laboratory by passing an electric current through dry melted sodium hydroxide. On the large scale the metal is also prepared by the electrolysis of melted sodium hydroxide. The details of this process were worked out by Hamilton Y. Castner. A cross-section of the apparatus is shown in Fig.

126. The positive electrode, A, and the negative, D, are immersed in melted sodium hydroxide, C. When the current is turned on, metallic sodium and hydrogen are set free at the surface of D, and, on account of its lightness, the sodium at once rises to the covered receiver, B, the hydrogen escaping through the cover. Oxygen is set free at the positive electrode, and escapes through the small holes indicated at E. A wire gauze is suspended between the two electrodes to prevent the possible mixing of the two gases.
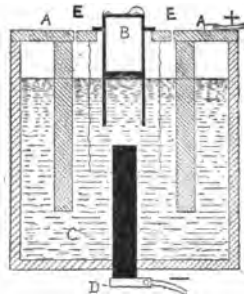
FIG. 126

Sodium could also be made by the reduction of the carbonate with charcoal:

$$Na_2CO_3 + 2\,C = 2\,Na + 3\,CO.$$
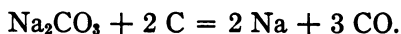
627. Uses. Metallic sodium is used as a reducing agent in the manufacture of certain organic compounds. It was at one time used as a reducing agent in the preparation of aluminum. It is also used as a dehydrating agent for the removal of the last traces of water from ether. Compounds of sodium are used for a great many different purposes, some of which will be mentioned later in connection with the description of the more important substances.

628. Common compounds. Sodium chloride, common salt, or **halite,** $NaCl$; **sodium hydroxide,** or **caustic soda,** $NaOH$; **sodium sulphate,** or **Glauber's salt,** $Na_2SO_4 \cdot 10\,H_2O$; **sodium carbonate,** or **soda ash,** Na_2CO_3; sodium carbonate, or **sal soda,** otherwise known as **washing-soda,** $Na_2CO_3 \cdot 10\,H_2O$; **hydrogen sodium carbonate, sodium bicarbonate, acid sodium carbonate,** also known as **baking-soda** or **saleratus,** $HNaCO_3$; sodium nitrate, or **Chili saltpetre,** $NaNO_3$.

629. The oxides of sodium. When sodium burns, a mixture of the two oxides Na_2O and Na_2O_2 is formed. Sodium oxide, Na_2O, may be made by the action of sodium on sodium nitrate. It is a white powder which unites violently with water, forming sodium hydroxide:

$$Na_2O + HOH = 2\,NaOH.$$

630. Sodium peroxide, Na_2O_2, is a white solid formed by heating sodium in an atmosphere of oxygen until it will take up no more of the gas.

It reacts with water with the formation of sodium hydroxide and oxygen:

$$2\,Na_2O_2 + 2\,HOH = 4\,NaOH + O_2.$$

Oxygen may be obtained by allowing water to drip on granulated sodium peroxide in some form of gas-generator.

When treated with acids the corresponding sodium salt is formed, together with hydrogen peroxide:

$$Na_2O_2 + 2\,HCl = 2\,NaCl + H_2O_2.$$

It is a powerful oxidizing and bleaching agent and is manufactured on a large scale.

Sodium chloride, or common salt (mineral name, **halite**), NaCl.

631. Occurrence. This substance is the commonest representative of the large class of compounds known as salts. It occurs in enormous quantities in various parts of the earth. The salt of the sea-water is largely sodium chloride. In this country a stratum of rock salt is found at a depth of from 800 to 1,000 ft. below the surface of the ground in central and western New York State, Michigan, West Virginia, Kentucky, and Louisiana.

Common salt crystallizes in cubes. When a salt solution evaporates slowly peculiar hollow, four-sided pyramids are formed, known as **hopper crystals** (Fig. 127).

One hundred parts of water dissolve 36 parts of salt at 0°, and only 39 parts at 100°; therefore it is not practicable to crystallize this substance by cooling a hot saturated solution.

Fig. 127

Salt crystals contain minute quantities of water mechanically enclosed, and when heated the steam from this water blows the crystal to pieces, producing a peculiar crackling sound called **decrepitation.**

632. Preparation. On account of its abundance in nature salt is never manufactured, but is obtained occasionally as a
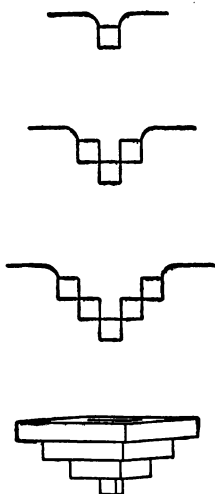
by-product in the manufacture of other substances. For example, sodium nitrate is combined with potassium chloride for the purpose of obtaining potassium nitrate, and common salt is obtained as a by-product:

$$NaNO_3 + KCl = KNO_3 + NaCl.$$
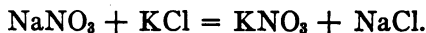
Salt is either mined in the solid form by ordinary mining methods or is obtained by the evaporation of brine or sea-water. The most insoluble impurities separate first and are removed, the precipitation of the salt then follows, and the most soluble impurities are left in the residual liquid. Salt for table use is further purified by fractional crystallization.
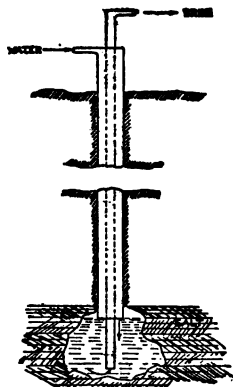
FIG. 128

In the case of the Solvay process, to be described in the next article, where the salt is required in solution, it is extremely economical and efficient to obtain it by forcing a stream of fresh water down to the salt stratum. The fresh water dissolves the salt and comes to the surface in the form of a saturated solution ready for use (Fig. 128.)

If it so happens that a fresh-water supply can be obtained sufficiently high up to give the pressure necessary to bring the heavier salt water to the surface, the process is still more efficient.

Sodium Carbonate, Soda, or Sal Soda

633. **Properties.** This substance is a colorless salt that crystallizes from water solution in the mono-clinic form with 10 molecules of water of crystallization. When exposed to the air the crystals rapidly lose some of their water (effloresce), and fall to a white powder.

The water solution of sodium carbonate reacts alkaline, for the reason that the salt is a compound of a strong base with a weak acid. It is hydrolyzed by the water, forming highly dissociated sodium hydroxide and slightly dissociated carbonic acid. The hydroxide ions, being in excess of the hydrogen ions, produce the alkaline reaction (250).

It reacts readily with all acids, producing a salt, water, and carbon dioxide. Its solution produces precipitates of the insoluble carbonates.

It is used in the manufacture of glass and soap, as well as for the preparation of many other compounds.

Sodium carbonate is manufactured by the **Solvay** and **Le-Blanc** processes and may also be made by passing a stream of carbon dioxide into a solution of sodium hydroxide.

634. The Solvay process consists in passing carbon dioxide into a strong solution of ammonia in salt water. The carbon dioxide unites with the ammonium hydroxide, forming ammonium bicarbonate. This reacts with the sodium chloride, forming sodium bicarbonate, which falls as a precipitate, because it is not as soluble as ammonium chloride in the strong solution used. The equations representing these reactions are as follows:

$$CO_2 + H_2O = H_2CO_3.$$
$$H_2CO_3 + NH_4OH = HNH_4CO_3 + H_2O.$$
$$HNH_4CO_3 + NaCl = HNaCO_3 + NH_4Cl.$$
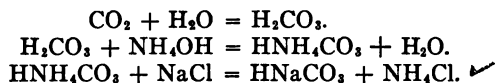
The process is continuous. The mass of fine crystals of the bicarbonate is separated by filtration and passes through long iron cylinders heated externally by producer gas. This not only dries the bicarbonate but also converts it to the dry normal carbonate, Na_2CO_3, which is called **soda ash:**

$$2\ HNaCO_3\ \text{heated} = Na_2CO_3 + H_2O + CO_2.$$

The carbon dioxide liberated is again passed through the carbonating towers. The liquid which runs through the filter contains all of the ammonia as ammonium chloride. The ammonia is recovered by mixing the filtrate with slaked lime and boiling with steam. It thus appears that the ammonia need never be used up but is utilized over and over again to bring about the desired reaction:

$$2\ NH_4Cl + Ca(OH)_2 = CaCl_2 + 2\ NH_3 + 2\ H_2O.$$

635. Diagram of Solvay process. Since by this process alone about 11,000 tons of sodium carbonate are produced daily in the world, it seems desirable to describe it a little more fully. The crude products necessary are limestone, water, and salt. The works can only be successful, then, in a region where these substances occur abundantly. With the help of the following sketch the whole process can be made clear (Fig. 129).

Limestone and coke are charged alternately into the top of the lime-kiln, A. The fire burns continuously in the middle of the kiln, giving off carbon dioxide both from the limestone and the coke. The gases are drawn from the top and by means of a suitable pump are forced into the bottom of the carbonating tower, B. This tower is filled with a saturated
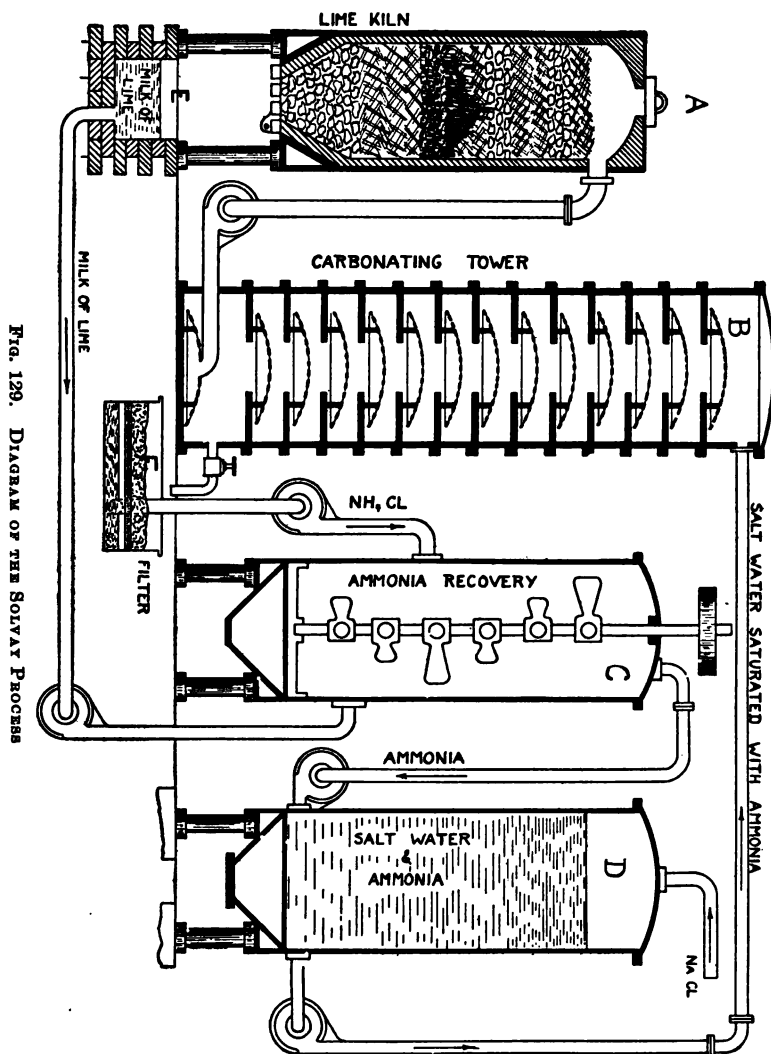
Fig. 129. Diagram of the Solvay Process

solution of common salt and ammonia. The carbon dioxide, rising through a great many perforated iron disks, comes in contact with a large surface of the liquid and is all converted to ammonium bicarbonate.
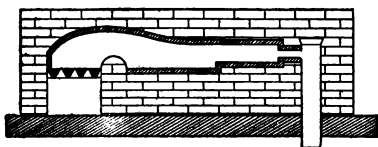
FIG. 130   .

The ammonium bicarbonate, acting on the sodium chloride, converts the latter to sodium bicarbonate. This is removed from the bottom of the tower and goes directly into a suitable filter, *F*. The partly dry bicarbonate goes into a roaster, not shown in this diagram, and is converted to normal carbonate. The filtrate, containing all of the ammonia as ammonium chloride, is pumped into an ammonia recovery apparatus, *C*, where it is digested with milk of lime. The milk of lime is made by slaking lime in a well near the base of the lime-kiln, *E*. As a result of being heated with calcium hydroxide, all of the ammonia is set free and is at once pumped into a new supply of saturated salt water in *D*. In turn, this solution of salt water and ammonia goes into the top of the carbonating tower, *B*. Calcium chloride, with all of the impurities from the lime and salt water, is discharged from the bottom of the apparatus *C*.

636. The LeBlanc process. In this process common salt is heated in a reverberatory furnace with exactly the proper quantity of sulphuric acid to form the normal sulphate and hydrochloric acid gas (Fig. 130):

$$2\,NaCl + H_2SO_4 = Na_2SO_4 + 2\,HCl.$$
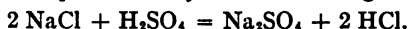
The sodium sulphate so produced is called **salt cake.** The salt cake is broken up and thoroughly mixed with carbon in the form of coal and limestone crushed to about the size of a small pea. This mixture is either heated in a reverberatory furnace, where the charge is stirred by hand, or in a rotary furnace, where it is automatically agitated (Fig. 131). The carbon reduces the sulphate to sulphide:

FIG. 131

$$Na_2SO_4 + 2\,C = Na_2S + 2\,CO_2.$$
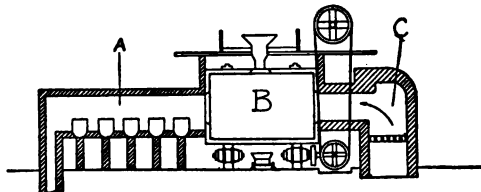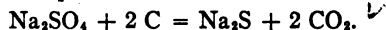
The sodium sulphide then reacts with the calcium carbonate to give sodium carbonate and calcium sulphide:

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

The product from this treatment, called **black ash,** is then treated with water, which dissolves all of the sodium carbonate. When this solution is concentrated the sodium carbonate crystallizes with 10 molecules of water, forming the familiar **sal soda,** or washing-soda.

Sodium carbonate could also be made by passing carbon dioxide into a solution of sodium hydroxide:

$$CO_2 + 2\,NaOH = Na_2CO_3 + H_2O.$$

637. Sodium bicarbonate, acid sodium carbonate, or hydrogen sodium carbonate. This substance is also known as baking-soda, or saleratus. It is a finely divided white crystalline powder and is obtained as the primary product in the Solvay process. When heated or dissolved in boiling water it is converted to normal sodium carbonate with the evolution of carbon dioxide:

$$2\,HNaCO_3 \text{ heated} = Na_2CO_3 + H_2O + CO_2.$$

The dry product formed in this way is the soda-ash of commerce. It is an ingredient of all effervescing medicines and tablets and is the source of the carbon dioxide in baking-powders.

It may be made by passing a stream of carbon dioxide through a solution of sodium carbonate or sodium hydroxide:

$$Na_2CO_3 + H_2O + CO_2 = 2\,HNaCO_3.$$
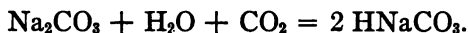
Sodium Hydroxide, or Caustic Soda, NaOH

638. Properties. Sodium hydroxide is a white solid that rapidly absorbs moisture from the air (deliquesces). It is very soluble in water, the solution being accompanied by the evolution of a large amount of heat.

Its water solution is extremely soapy to the taste and feeling.

It is a strong base, being highly dissociated in water solution. It neutralizes all acids and acid anhydrides, forming the corresponding sodium salts.

It is used largely in the manufacture of soap. For this purpose it is boiled with animal and vegetable fats and oils. The sodium unites with the organic acid of the fat, forming a salt which constitutes the soap, and glycerine is set free. An equation sufficient to represent this reaction follows:

$$3\,NaOH + \underset{\text{glycerine tristearate}}{C_3H_5(C_{17}H_{35}CO_2)_3} = \underset{\text{sodium stearate}}{3\,NaC_{17}H_{35}CO_2} + \underset{\text{glycerine}}{C_3H_5(OH)_3}.$$
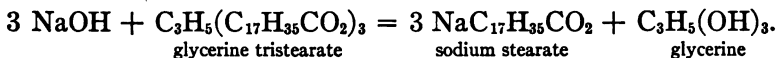
639. Manufacture. A cheap method for making this substance is to treat a solution of sodium carbonate with an excess of milk of lime:

$$Na_2CO_3 + Ca(OH)_2 = \underline{CaCO_3} + 2\,NaOH.$$
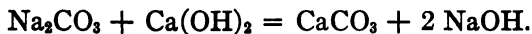
After the action is over the calcium carbonate is allowed to settle and the solution of caustic soda is evaporated, at first in vacuum pans and finally in open iron pots.

640. The Castner process. It would seem to be a very simple matter to produce sodium hydroxide by the electrolysis of sodium chloride solution. This would give free chlorine at the positive electrode and sodium hydroxide and hydrogen at the negative. When this is tried, however, some of the chlorine invariably unites with some of the sodium hydroxide, forming
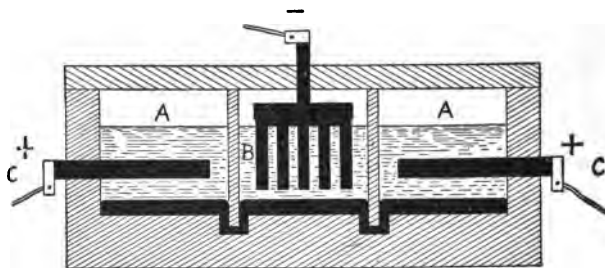
Fɪɢ. 132

hypochlorites. The problem was to get some arrangement that would absolutely prevent the chlorine from coming in contact with the sodium hydroxide. This was solved by Castner, as shown in Fig. 132. The cell is divided into three compartments by two hanging partitions which extend into two corresponding depressions in the bottom. The whole bottom is covered with a layer of mercury. This effectually prevents any liquid passing from one compartment to another. The end compartments, *A*, containing the positive carbon electrodes, *C*, are filled with brine. The middle compartment, containing the iron negative electrode, *B*, is filled with sodium hydroxide solution. By suitable mechanical means the mercury is kept circulating from the compartments *A* through the middle compartment and back again.

When the current is flowing chlorine is given off at the electrodes in *A* and is carried off to lime absorbers where it is converted to chloride of lime, or perhaps liquefied in iron cylinders for shipment. The sodium forms an amalgam with

the mercury, and is soon carried into the middle compartment, where it is converted to sodium hydroxide with the evolution of hydrogen.

Very pure sodium hydroxide is made by the action of steam on pure metallic sodium. This product, however, is very expensive compared with that produced by either of the above processes.

641. Sodium sulphate, Glauber's salt, $Na_2SO_4.10 H_2O$.

Sodium sulphate is a colorless salt that crystallizes with several different amounts of water. The best known is the form containing 10 molecules of water of crystallization known as Glauber's salt.

When exposed to the air Glauber's salt rapidly loses some of its water (effloresces) and falls to a white, amorphous powder.

Sodium sulphate is most soluble at a temperature of 33°. If a saturated solution of this substance be made at this temperature and carefully filtered into a clean vessel, the excess of the salt will not crystallize out on cooling but will remain in the supersaturated condition.

A minute crystal of Glauber's salt, or even a little dust, will at once bring about crystallization and the whole mass of liquid will apparently solidify.

Sodium sulphate is used in medicine and in the manufacture of sodium carbonate by the LeBlanc process.

642. Acid sodium sulphate, $HNaSO_4$. When sulphuric acid reacts with almost any sodium salt, sodium sulphate and another acid are formed. This reaction usually takes place in two stages, the acid salt being first formed:

$$NaCl + H_2SO_4 = HNaSO_4 + HCl.$$
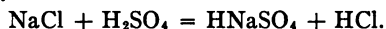
If the acid salt, then, be mixed with more of the salt and heated to a much higher temperature, the normal salt with more of the volatile acid is produced:

$$NaCl + HNaSO_4 = Na_2SO_4 + HCl.$$
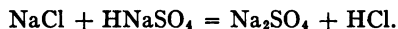
643. Sodium thiosulphate, $Na_2S_2O_3 \cdot 5 H_2O$. This compound was formerly and incorrectly called **hyposulphite** of soda and is still known to all photographers as **hypo**. It is used by them in the fixing solution on account of its ability to dissolve the halogen salts of silver. It is a good reducing agent and is readily oxidized by chlorine and iodine to **sodium tetrathionate,** $Na_2S_4O_6$:

$$2 Na_2S_2O_3 + I_2 = 2 NaI + Na_2S_4O_6.$$
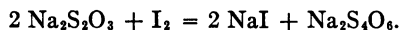
For this reason it is used as an **antichlor,** that is, for the purpose of removing the last traces of the bleaching agent when a material has been bleached by the use of chlorine.

When treated with an acid the corresponding sodium salt is formed,

together with the precipitation of sulphur and the evolution of sulphur dioxide:

$$Na_2S_2O_3 + 2\,HCl = 2\,NaCl + \underline{S} + H_2O + SO_2.$$

644. Sodium nitrate, or Chili saltpetre, $NaNO_3$. This is a colorless salt which derives its name, **Chili saltpetre,** from the fact that extensive deposits are found in Chili.

At present it is the chief source of the nitrates used in the fertilizer industry. Much of it is converted to potassium nitrate by double decomposition with potassium chloride. It is also one of the chief sources of nitric acid, which is obtained by heating it with sulphuric acid:

$$2\,NaNO_3 + H_2SO_4 = Na_2SO_4 + 2\,HNO_3.$$
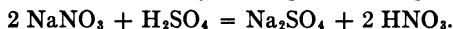
Potassium (Laboratory Exercise No. 31)

645. Appearance and occurrence. Potassium is a silver-white metal resembling sodium. It does not occur in the free condition, but is found in large quantities as silicates, such as **feldspar** and **mica.** It also occurs in large deposits in the form of potassium chloride.

646. Physical properties. It is a soft metal easily cut with a knife. It has a specific gravity of .875, melts at 62.5°, and boils at 720°. When it or its compounds are heated in the Bunsen flame, it produces a purple flame which appears red through a blue glass.

647. Chemical properties. When the metal is freshly cut, the brilliant, silver-white surface remains but a moment, being instantly tarnished by the formation of potassium hydroxide from the moisture of the air.

When burned, the chief product is potassium tetroxide, K_2O_4, which reacts violently with water, forming potassium hydroxide and oxygen.

The oxide K_2O may be made by careful heating of the metal with the proper quantity of oxygen.

When the metal is thrown on water the heat generated is sufficient to ignite the hydrogen, which burns with a purple flame:

$$2\,K + 2\,HOH = 2\,KOH + H_2.$$
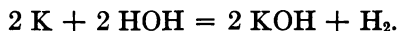
In general, the chemical properties of potassium are similar to those of sodium, it being, however, chemically more active than the latter.

Test. Potassium and its compounds color the Bunsen flame purple. When viewed through the blue glass this purple color appears red.

648. Preparation. It was first made by Davy in 1817 by the electrolysis of potassium hydroxide, and it is manufactured to-day in the same way that sodium is made.

649. Uses. The element itself has no especial use in the free condition. Its compounds, however, are of the utmost importance. Potassium in some form is indispensable in fertilizers. Most of the supply for this purpose is derived from the salt deposits at Stassfurt, where it occurs in the form of the chloride. One of the great problems of the technical chemists to-day is to discover a method of obtaining soluble compounds of potassium from the insoluble feldspar, abundant supplies of which are found in this country.

650. Common compounds. Potassium hydroxide, or caustic potash, KOH; **potassium nitrate,** or saltpetre, KNO_3; **potassium chlorate,** $KClO_3$; **potassium carbonate,** or pearlash, K_2CO_3.

651. Potassium hydroxide, or caustic potash, KOH. This is a white solid resembling sodium hydroxide, so much so that the pupil would have some trouble in distinguishing between them. It **deliquesces** rapidly in the air, *i. e.*, absorbs water, and, if left exposed, ultimately is converted entirely to the carbonate by the absorption of carbon dioxide.

It is a strong base, having a soapy taste and feeling and neutralizes all acids.

Potassium hydroxide may be made by the same processes used in the preparation of sodium hydroxide. The carbonate treated with calcium hydroxide gives potassium hydroxide and calcium carbonate. The potassium hydroxide may be treated with alcohol, which dissolves it readily and thereby separates it from most of the impurities. After the evaporation of the alcohol the hydroxide is obtained in a fairly pure form. This is cast in the form of sticks and marked **potassium hydroxide, pure by alcohol.**

It may also be made by the Castner process described under sodium. Potassium hydroxide is used in the laboratory for absorbing water and carbon dioxide. It is also used for the manufacture of potassium soaps and many other potassium compounds.

652. Potassium nitrate, or saltpetre, KNO_3. Potassium nitrate is formed in small quantities wherever decaying nitrogenous matter comes in contact with potassium compounds. It does not occur, however, in sufficiently large quantities to pay for collecting. It is prepared chiefly

by the double decomposition of potassium chloride with sodium nitrate. Although all of the compounds involved in this change are soluble, when the solution is concentrated sodium chloride first separates, leaving a solution of potassium nitrate.

The hot mother-liquor is decanted and on cooling deposits crystals of potassium nitrate.

Large quantities of potassium nitrate are used in the manufacture of **black gunpowder.** For this purpose 75 parts of the nitrate are mixed with 10 parts of sulphur and 15 parts of charcoal.

When this kind of powder is fired a white smoke is formed, which probably contains potassium carbonate and sulphide.

Treated with sulphuric acid, potassium nitrate gives potassium sulphate and nitric acid:

$$KNO_3 + H_2SO_4 = HKSO_4 + HNO_3.$$
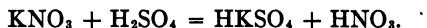
Mixed with wood or charcoal and ignited, it produces a violent combustion, with the formation of potassium carbonate, nitrogen, and carbon dioxide:

$$4 KNO_3 + 5 C = 2 K_2CO_3 + 3 CO_2 + 2 N_2.$$

653. Potassium carbonate, K_2CO_3. The woody fibre of all land plants contains potassium. When the plant is burned the potassium oxide formed combines with some of the carbon dioxide, forming potassium carbonate. Much potassium carbonate, called **potash,** was formerly obtained by boiling wood-ashes in iron pots with water. After the insoluble residue had settled, the liquid was drawn off and evaporated.

Potassium carbonate is a white powder that absorbs moisture from the air (deliquesces) and is very soluble. Like sodium carbonate its water solution reacts strongly alkaline.

It is manufactured by the LeBlanc process from potassium chloride.

Crude potassium carbonate is a valuable source of potash for fertilizers and much is used for that purpose.

654. Potassium chlorate, $KClO_3$. This substance was early introduced to the student as a source of oxygen. It crystallizes in well-formed, flat crystals of the mono-clinic variety. When heated sufficiently it gives up all of its oxygen, forming potassium chloride:

$$2 KClO_3 \text{ heated} = 2 KCl + 3 O_2.$$
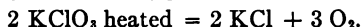
This reaction takes place at a much lower temperature if it be mixed with an equal bulk of powdered manganese dioxide, which simply acts as a **catalytic agent,** *i. e.,* aiding the reaction but undergoing no change itself.

Potassium chlorate could be made by passing chlorine into a solution of potassium hydroxide:

$$3 Cl_2 + 6 KOH = KClO_3 + 5 KCl + 3 H_2O.$$

This method is not very efficient, on account of the large amount of potassium chloride formed. It is better first to form calcium chlorate

by passing chlorine into calcium hydroxide, then treating this with potassium chloride:

$$Ca(ClO_3)_2 + 2 KCl = CaCl_2 + 2 KClO_3.$$
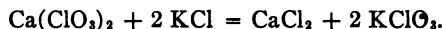
Potassium chlorate is a powerful oxidizing agent and when mixed with any combustible substance may produce violent explosions.

It is used for the purpose of generating oxygen, in explosives, match compositions; and in solution in water as a gargle for sore throat. It is an endothermic compound and in large quantities may be made to explode with great violence.

655. Potassium sulphate, K_2SO_4. Unlike sodium sulphate potassium sulphate crystallizes without water of crystallization. It is used in the preparation of potassium carbonate and potash alum.

656. Potash alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24 H_2O$. If 1 molecular weight of potassium sulphate be dissolved with 1 molecular weight of aluminum sulphate, on filtering and crystallizing perfect crystals of the above compound separate.

This substance is simply one example of a large class of compounds called **alums** having the general formula, $R_2SO_4 \cdot M_2(SO_4)_3 \cdot 24 H_2O$, in which R is a univalent element, like sodium, potassium, or ammonium, and M is a trivalent element, like ferric iron, aluminum, or chromium.

Potash alum is the common alum, and is used as a **mordant** in dyeing. A **mordant** is a substance into which a piece of cloth is dipped previously to dyeing, for the purpose of making the color adhere to the fibres.

Ammonium

657. Ammonium, NH_4, is an imaginary compound of nitrogen and hydrogen which forms salts with the acid radicals similar to the salts of the alkali metals. For this reason it is classed with sodium and potassium, and also for the reason that unless so classed the ammonium compounds might not receive proper attention.

Ammonia gas, NH_3, unites directly with the acids, forming ammonium salts:

$$NH_3 + HCl = NH_4Cl.$$

When ammonium salts are dissolved in water they give the ammonium ion, NH_4^+. When ammonia gas is passed into water it is very readily dissolved and much heat is generated. The solution contains some ammonium hydroxide,

$$NH_3 + HOH \leftrightarrows NH_4OH,$$

although it is probable that much of the ammonia remains simply dissolved.

658. Ammonium chloride, sal ammoniac, NH_4Cl.   Ammonium chloride is made by neutralizing the ammonia gas from the ammoniacal liquor of gas-works with hydrochloric acid.   The crude product is purified by sublimation.

It may also be made by evaporating a mixture of ammonium sulphate and sodium chloride solutions.   On cooling the concentrated solution, ammonium chloride separates first, leaving the more soluble sodium sulphate in solution:

$$(NH_4)_2SO_4 + 2\ NaCl = Na_2SO_4 + 2\ NH_4Cl.$$
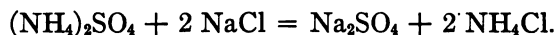
When ammonium compounds are heated they are almost completely dissociated into ammonia and the corresponding acid; when these hot gases reach a cooler portion of the apparatus they recombine to form the ammonium salt.   Thus ammonium salts apparently sublime when heated.   This fact makes it easy to distinguish them from metallic salts.

In order to obtain ammonia from an ammonium salt it is only necessary to heat the latter with a base or a basic oxide. The base combines with the acid and the ammonia is set free:

$$NH_4Cl + NaOH = NaCl + NH_3 + H_2O.$$

659. Ammonium carbonate, $(NH)_2CO_3$.   If carbon dioxide be passed into ammonium hydroxide until no more is absorbed, ammonium bicarbonate is formed:

$$CO_2 + NH_4OH = HNH_4CO_3.$$

If this solution be treated with a second volume of ammonium hydroxide equal to the original, the normal salt is formed in solution:

$$HNH_4CO_3 + NH_4OH = (NH_4)_2CO_3 + H_2O.$$
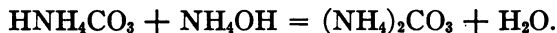
It is a white solid that rapidly gives off ammonia and leaves the bicarbonate.

The ammonium carbonate used in the laboratory is a mixture of ammonium bicarbonate and ammonium carbamate, $HNH_4CO_3NH_4NH_2CO_2$.

660. Ammonium sulphide, $(NH_4)_2S$.   This reagent is much used in the laboratory for precipitating certain sulphides.   It is made by passing hydrogen sulphide into a solution of ammonium hydroxide, until the latter is saturated with the gas.

This produces hydrogen ammonium sulphide. A bulk of ammonium hydroxide equal in volume to the original is now added, converting the acid salt to the normal:

$$H_2S + NH_4OH = HNH_4S + HOH.$$
$$HNH_4S + NH_4OH = (NH_4)_2S + HOH.$$
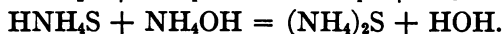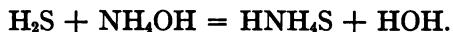
The solution is almost colorless at first, but is unstable and constantly gives off ammonia and hydrogen sulphide. Owing to the slow oxidation of the hydrogen sulphide, sulphur is set free, which dissolves in the solution, coloring it yellow.

Yellow ammonium sulphide is made by dissolving flowers of sulphur in the colorless solution. On long standing much of the sulphur is precipitated.

CHAPTER XLII

THE ALKALINE EARTH METALS

Calcium, Strontium, and Barium

Calcium (Laboratory Exercise No. 32)

661. Appearance and occurrence. Calcium is a silver-white metal that does not occur in the free condition but is found abundantly as the carbonate, $CaCO_3$, in many different forms, among which are **marble, limestone, chalk, coral,** and **sea-shells.** It is also found in the form of sulphate, **gypsum,** $CaSO_4 \cdot 2\ H_2O$, and in many silicates.

662. Physical properties. It is a little harder than lead and may be rolled into sheets and drawn out into wire. It has a specific gravity of 1.85, and melts at 760°.

663. Chemical properties. In dry air it is quite inactive, but when heated sufficiently it burns in air or oxygen, forming calcium oxide:

$$2\ Ca + O_2 = 2\ CaO.$$
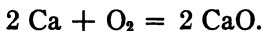
When burned in air the product is contaminated with some **calcium nitride,** Ca_3N_2, formed by the metal combining with the nitrogen of the atmosphere.

The metal also unites with hydrogen and the halogens, and reacts energetically with water, giving calcium hydroxide and hydrogen:

$$Ca + 2\ H_2O = Ca(OH)_2 + H_2.$$
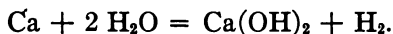
664. Test. Calcium compounds, moistened with hydrochloric acid, impart a dull-red color to the flame. The pupil may have some difficulty in distinguishing calcium compounds from strontium, for the reason that the latter also colors the flame red. Strontium sulphate is very insoluble, while calcium sulphate is appreciably soluble. Therefore strong calcium salt solutions give a precipitate of the sulphate when a soluble sulphate is added, while weak solutions do not.

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665. Preparation. Not many years ago calcium was a laboratory curiosity listed in the catalogues at ten dollars a gram.
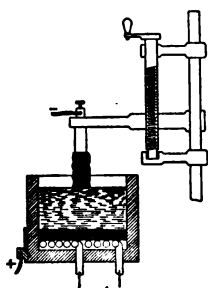
FIG. 133

It is made now quite easily by the electrolysis of melted calcium chloride. As fast as the metal is deposited on the negative electrode the latter is withdrawn from the electrolyte by a suitable screw arrangement, thus forming a bar of calcium which may reach several feet in length (Fig. 133). The excess of heat is removed by a stream of water kept circulating through a pipe coiled in the bottom of the graphite crucible.

666. Uses. The element itself is a powerful reducing agent. Its uses at present are not numerous, but if produced at a low enough cost it may become of great importance in some of the large industries.

667. Common compounds. Calcium oxide, or **lime**, CaO; calcium hydroxide, or **slaked lime**, Ca(OH)$_2$; calcium chloride, CaCl$_2$; **chloride of lime**, CaOCl$_2$; **calcium phosphates**, Ca$_3$(PO$_4$)$_2$, HCaPO$_4$, H$_4$Ca(PO$_4$)$_2$; **calcium carbonate**, CaCO$_3$; calcium sulphate, or **gypsum**, CaSO$_4$·2 H$_2$O.

668. Calcium oxide, or lime. This is a white amorphous solid formed by heating calcium carbonate, in the form of marble or limestone, in an apparatus called a **lime-kiln** (Fig. 134). A lime-kiln is usually arranged so that the fuel and limestone may be alternately and continuously

FIG. 134

charged in at the top and the lime removed at the bottom. The fuel used may be wood, charcoal, or coke.
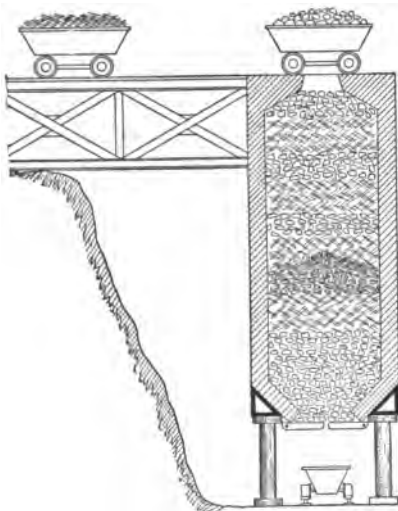
Lime is very infusible and when heated to the temperature

of the oxyhydrogen flame it gives out an intensely white light. This is known as the **limelight.**

When moistened with water it soon swells up and falls to a dry white amorphous powder known as **slaked lime** or calcium hydroxide.

This change is accompanied by the evolution of a large amount of heat. A lump of lime left exposed to the air for some time is slowly converted to a dry white amorphous powder consisting entirely of carbonate, known as **air-slaked lime.** This is due to the combined absorption of both water and carbon dioxide from the air. Lime is so prone to do this that bottles filled with lumps must be very tightly corked and the cork covered with paraffine or the absorption of water and carbon dioxide through the cork will cause the lumps to swell and burst the bottle.

Lime is used most extensively in the manufacture of mortar and cement, but it is also one of the crude materials used in the manufacture of glass and cast iron, and for the linings of Bessemer and open-hearth steel furnaces.

669. Calcium hydroxide, or **slaked lime,** $Ca(OH)_2$, as has already been stated, is the dry white amorphous powder obtained when calcium oxide is mixed with the proper quantity of water:

$$CaO + HOH = Ca(OH)_2.$$

The reaction is accompanied by the evolution of a large amount of heat, sufficient to boil away some of the excess water. The powder, mixed with water to form a thin paste, is known as **milk of lime,** and a saturated solution of it, best formed by filtering thin milk of lime, is known as **lime-water.**

Dry slaked lime absorbs carbon dioxide from the air when exposed, and is soon completely converted to calcium carbonate.

Calcium hydroxide is only slightly soluble in water, but the solution is strongly basic. It is used in the preparation of mortar, in which it is mixed with sand; of sodium hydroxide, by mixing it with sodium carbonate; and for the liberation of ammonia from ammonium compounds. It absorbs chlorine readily, forming what is known as **chloride of lime.**

670. **Mortar** is a mixture of sand and slaked lime, used in laying up brick and stone walls above ground. When it is to be used for plastering on walls a certain amount of hair is worked into it to give it greater strength. The initial hardening is due simply to its drying. In the course of time enough carbon dioxide finds its way through it to convert all of the calcium hydroxide to carbonate, thereby increasing its hardness. It is reasonable also to assume that some of the sand is converted to calcium silicate.

671. **Calcium chloride,** $CaCl_2$, is the white amorphous and porous substance obtained when pure calcium carbonate or lime is dissolved in hydrochloric acid and the solution evaporated to dryness. In this form it is extremely deliquescent, *i. e.*, absorbs water, and fine particles left exposed soon appear as little globules of liquid.

When the dry salt is dissolved in water much heat is generated. Solutions of calcium chloride, when evaporated, deposit crystals containing 6 molecules of water. The crystallized salt dissolves in water with the absorption of heat, and when mixed with cracked ice produces a very efficient freezing mixture.

Calcium chloride in the nearly anhydrous and porous condition is much used in the laboratory as a drying agent for those gases that do not combine with it. Ammonia gas forms a compound with it and therefore should be dried by passing it through a tube filled with lime.

For filling drying tubes (Fig. 135) the calcium chloride is granulated to the required size and sifted free from dust. After filling the tubes a loose plug of cotton is inserted to prevent particles of the chloride from being blown out by a sudden rush of gas.

FIG. 135

Calcium chloride, on account of its tendency to absorb water, makes a good dust-preventive for use on roads. A crude variety is used for this purpose in many sections of the country. It is sprinkled on, either in solution or in the granulated form. It not only prevents the water from evaporating but actually causes moisture to condense on the roadway.

672. Calcium carbide, CaC_2, is the well-known compound used for the production of acetylene gas by the addition of water. It is made by heating lime and carbon to a very high temperature in an electric furnace. When treated with water calcium hydroxide and acetylene are formed:

$$CaC_2 + 2\,HOH = Ca(OH)_2 + C_2H_2.$$
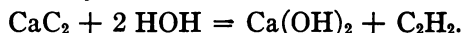
673. Chloride of lime, or **bleaching-powder,** $CaOCl_2$, is the moist amorphous powder sold by the druggists as a deodorizer and disinfectant.

It gradually gives off free chlorine, which is a powerful oxidizing agent, capable of destroying germs of disease and

oxidizing disagreeable odors. It is made by allowing chlorine to come in contact with slaked lime. This is accomplished at present by a continuous process in an apparatus consisting of a series of horizontal cylinders placed one above the other. The slaked lime enters at the top and the chlorine gas at the bottom. The
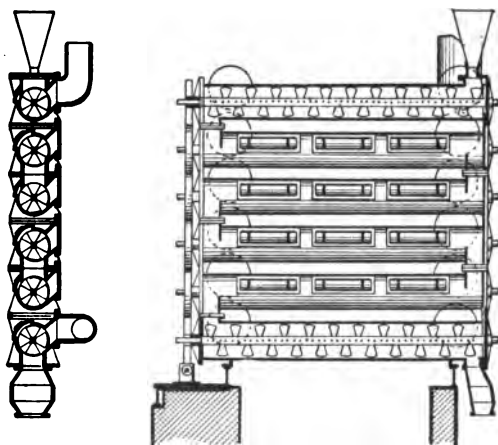
From Thorp's "Outlines of Industrial Chemistry," by permission of The Macmillan Company

FIG. 136

lime is caused to move back and forth through all of the cylinders by revolving conveyors until it emerges at the bottom saturated with chlorine (Fig. 136).

Bleaching-powder is much used for bleaching cotton cloth. For this purpose the cloth is passed continuously by means of rolls through a series of tanks containing bleaching-powder solution, dilute hydrochloric acid, an **antichlor** such as sodium thiosulphate, and water for washing (Fig. 70).

674. Calcium phosphate, $Ca_3(PO_4)_2$. Normal, or tertiary, calcium phosphate occurs in nature as **phosphorite** in many localities, especially

in Florida. It is also the chief mineral constituent of bones. After all of the organic matter and carbon in bones has been burned away the white mineral residue, known as **bone-ash,** is almost pure calcium phosphate, $Ca_3(PO_4)_2$. It is used chiefly in the manufacture of fertilizers, but is also the crude material from which phosphorus and phosphoric acid are prepared.

Since the normal phosphate is almost completely insoluble in water, it would be of little value as a fertilizer ingredient. It is therefore treated with sulphuric acid to convert it to **primary calcium phosphate,** which is soluble in water. For this purpose enough sulphuric acid is added to combine with 2 of the atoms of calcium, forming 2 molecules of calcium sulphate:

$$Ca_3(PO_4)_2 + 2 H_2SO_4 = H_4Ca(PO_4)_2 + 2 CaSO_4.$$
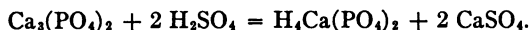
No attempt is made to separate the calcium sulphate from the primary calcium phosphate, but the two compounds together form a dry white powder known as **acid phosphate.** This acid phosphate is used either in the pure form by itself to add phosphoric acid to the soil or combined with materials furnishing nitrogen and potash, both of which are necessary in a complete fertilizer.

The **normal, tertiary,** or **tri-calcium phosphate** may be prepared in the precipitated form by adding a solution of sodium phosphate to a solution of a calcium salt:

$$3 CaCl_2 + 2 HNa_2PO_4 \leftrightarrows Ca_3(PO_4)_2 + 4 NaCl + 2 HCl.$$
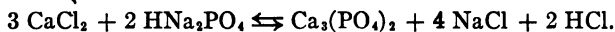
675. Calcium carbonate, $CaCO_3$. Calcium carbonate is very abundant and exists in several different and common forms. **Limestone** is the commonest form and is abundantly distributed over the earth. **Marble** is nothing but a mass of minute crystals of calcium carbonate often colored by traces of impurities. Single crystals of the mineral are known as **calcite,** and· when these are found in very large and transparent form they are known as **Iceland spar.** **Dolomite** is made up of calcium carbonate and magnesium carbonate, and resembles marble. **Chalk** is composed of microscopic shells of minute organisms. The cliffs on the south coast of England consist of chalk. **Blackboard crayon** is commonly made of plaster of Paris and should not be confused with chalk.

Oyster and clam shells, sea-shells in general, as well as coral, consist chiefly of calcium carbonate.

676. Properties of calcium carbonate. Calcium carbonate, when heated, is converted to calcium oxide, or lime, CaO, and carbon dioxide:

$$CaCO_3 \text{ heated} \leftrightarrows CaO + CO_2.$$
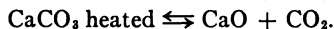
This reaction is never complete unless the carbon dioxide can escape. Calcium carbonate is readily dissolved by hydrochloric, nitric, and acetic acids:

$$CaCO_3 + 2 HCl = CaCl_2 + H_2O + CO_2.$$
$$CaCO_3 + 2 HNO_3 = Ca(NO_3)_2 + H_2O + CO_2.$$
$$CaCO_3 + 2 HC_2H_3O_2 = Ca(C_2H_3O_2)_2 + H_2O + CO_2.$$
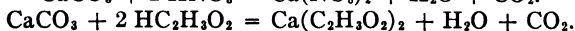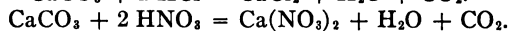
Also, water containing carbon dioxide dissolves it quite readily. In this case an acid carbonate which is soluble is supposed to be formed:

$$CaCO_3 + H_2O + CO_2 = CaH_2(CO_3)_2.$$

When this solution is heated the carbon dioxide is driven off, and a precipitate of the normal carbonate is formed. Precipitated calcium carbonate may be readily prepared by adding a solution of sodium carbonate to the solution of a calcium salt:

$$CaCl_2 + Na_2CO_3 = \underline{CaCO_3} + 2\,NaCl.$$
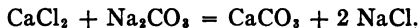
This product, when thoroughly washed, is known as **precipitated chalk.** It is much used in the preparation of tooth-powders.

677. **Limestone caves.** Water is a great solvent; and spring water always contains in solution varying quantities of the various rocks with which it has been in contact. Water containing carbon dioxide dissolves limestone quite readily. In the past geological ages flowing water has dissolved out great caverns in the limestone formation at various places on the earth. Examples of such caves are the **Mammoth Cave in Kentucky** and **Wier's Cave in Virginia.** In later times water containing dissolved calcium carbonate has dripped from the roofs of such caves, gradually depositing calcium carbonate as the water evaporates. This results in the formation of **stalactites** suspended from the roof, while **stalagmites** rise from the floor. In the course of time the stalactite grows until it meets the stalagmite, forming a pillar (Fig. 137).

678. **Hard water.** Water containing dissolved salts of calcium and magnesium is said to be **hard.** Almost all spring and well waters are "hard" in this sense. When soap is used in such water a certain amount of the soap is used up in precipitating all of the calcium and magnesium before it is possible to form suds. This is because the soap is a soluble salt of sodium or potassium with stearic or palmitic acid. When a solution of soap is put into hard water an insoluble calcium or magnesium soap is at once formed:

$$2\,NaC_{17}H_{35}CO_2 + CaSO_4 = \underline{Ca(C_{17}H_{35}CO_2)_2} + Na_2SO_4.$$
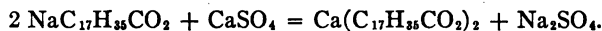
Water containing only carbonates is said to possess **temporary hardness,** because, when boiled, the excess of carbon dioxide escapes, and the carbonate is thrown out of solution. The process of removing the hardness is called **softening.** Water of temporary hardness may be softened either by boiling or by adding calcium hydroxide to precipitate the carbonate.

Water of permanent hardness contains salts of calcium or magnesium other than the carbonates, especially the sulphate or perhaps the chloride. Such water cannot be softened by boiling and is usually treated with sodium carbonate.

Great care should be used in selecting a water supply for steam-boilers, for, if it is a hard water, boiler scale is sure to form on the inside of the boiler and not only decrease its efficiency but may cause an explosion.

FIG. 137. STALACTITES AND STALAGMITES IN THE GREAT ADELSBERG GROTTO

679. Calcium sulphate, $CaSO_4$. Calcium sulphate occurs in nature in several different forms. The mineral known as **anhydrite** is calcium sulphate crystallized without water of crystallization. Combined with 2 molecules of water it is known as **gypsum,** $CaSO_4 \cdot 2\,H_2O$. This mineral is found in abundant quantities in several parts of the United States; also it occurs in large quantities in Nova Scotia. When gypsum occurs in masses made up of very small crystals it is known as **alabaster.**

680. Plaster of Paris. When gypsum is heated to a temperature of about 111° it loses approximately three quarters of its water of crystallization and falls to a dry white amorphous powder known as **plaster of Paris.** If this powder be mixed to a thick paste with water, it soon hardens, or **sets.** This is due to the fact that the partly dehydrated mineral combines with some of the water to reform the gypsum, thereby cementing the whole mass together.

Plaster of Paris is used in the making of plaster casts, ornamental plaster decorations, and the hard white surfaces of plastered walls. It is rather soluble and should not be used in places where it is likely to come in contact with water.

Strontium

681. Appearance and occurrence. Strontium is a silver-white metal resembling calcium. It does not occur in the free condition, but is found in comparatively small quantities as **strontianite,** $SrCO_3$, and as **celestite,** $SrSO_4$.

682. Properties. The metal has a specific gravity of 2.5 and melts at about 900° C. The sulphate is almost insoluble; therefore the addition of a soluble sulphate to a solution of a strontium salt produces a precipitate of the sulphate. Volatile compounds of strontium color the flame a brilliant red.

683. Preparation and uses. The metal may be prepared by electrolyzing the fused chloride. On account of the brilliant red color they give to the flame, strontium compounds, especially the nitrate, are used in the manufacture of fireworks.

684. Test. A small portion of the dry substance should be moistened with hydrochloric acid and introduced into the Bunsen flame. A red color indicates strontium or calcium. Another small portion is then dissolved in the smallest possible quantity of nitric acid, very much diluted with water, and sulphuric acid or a dissolved sulphate added. A white precipitate indicates strontium.

685. Common compounds. Strontium oxide, SrO; **strontium nitrate,** $Sr(NO_3)_2$; **strontium chloride,** $SrCl_2$; **strontium carbonate,** or strontianite, $SrCO_3$; and strontium sulphate, or **celestite,** $SrSO_4$; strontium hydroxide, $Sr(OH)_2 \cdot 8\,H_2O$.

Barium

686. Appearance and occurrence. Barium is a silver-white metal resembling calcium and strontium. It is never found in the free condition, but occurs chiefly in the form of the sulphate, known as **barite, or heavy spar**, $BaSO_4$, and as the carbonate, known as **witherite**, $BaCO_3$.

687. Properties. The metal has a specific gravity of 3.75, melts at 850° C., and boils at 950° C. All of the common compounds of barium are soluble except the carbonate, sulphate, and chromate. The soluble salts are poisonous.

A soluble sulphate, or sulphuric acid, added to a solution of a barium compound produces a white precipitate of the sulphate which is insoluble in dilute hydrochloric acid:

$$Ba(NO_3)_2 + K_2SO_4 = \underline{BaSO_4} + 2\ KNO_3.$$
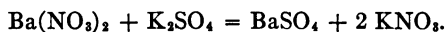
If a solution of a chromate or a dichromate be added to a solution of a barium salt, a yellow precipitate of barium chromate is formed: ˙

$$K_2CrO_4 + BaCl_2 = \underline{BaCrO_4} + 2\ KCl.$$

In the case of the dichromate, it should be remembered that the latter is the same as a chromate with 1 additional molecule of chromic anhydride,

$$K_2Cr_2O_7 \leftrightarrows K_2CrO_4 + CrO_3,$$

and that this molecule of CrO_3 in the presence of water constitutes 1 molecule of chromic acid, H_2CrO_4. Therefore the equation for the reaction would be:

$$K_2Cr_2O_7 + H_2O + 2\ Ba(NO_3)_2 = 2\ \underline{BaCrO_4} + 2\ HNO_3 + 2\ KNO_3.$$
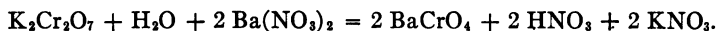
688. Test. Soluble barium compounds color the Bunsen flame green. A solution of such a compound, made slightly acid with HCl, gives no precipitate when hydrogen sulphide gas is passed through it; but gives a white precipitate of barium sulphate when sulphuric acid or a solution of a soluble sulphate is added, and a yellow precipitate when a solution of a chromate or dichromate is added.

689. Preparation and uses. The metal may be prepared by electrolyzing fused barium chloride. In the metallic form the element has no use except perhaps as a specimen in the show-case. Barium hydroxide solution is used in the refining of beet sugar and as an absorbent of carbon dioxide in the laboratory. Barium chloride is much used in the laboratory as a reagent for detecting the presence of the sulphate ion. Barium sulphate in the form of pulverized heavy spar is used as an adulterant in paint and as a weighting and filling material in the manufacture of paper.

690. Common compounds. Barium oxide, BaO; **barium dioxide**, BaO_2; **barium hydroxide**, $Ba(OH)_2 \cdot 8\ H_2O$; **barium nitrate**, $Ba(NO_3)_2$; **barium**

chloride, $BaCl_2 \cdot 2 H_2O$; **barium sulphate**, $BaSO_4$, also called **barytes** and **heavy spar.**

Barium oxide. This compound may be prepared in the pure form by heating the nitrate:

$$2 Ba(NO_3)_2 \text{ heated} = 2 BaO + 4 NO_2 + O_2.$$
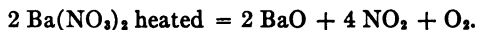
Barium dioxide, BaO_2. Barium dioxide may be made by heating barium monoxide in air or oxygen. When treated with dilute acids at a low temperature hydrogen peroxide is formed:

$$BaO_2 + H_2SO_4 = \underline{BaSO_4} + H_2O_2.$$
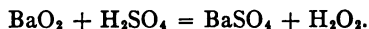
691. Barium hydroxide, $Ba(OH)_2 \cdot 8 H_2O$. This is the most soluble of the hydroxides of the alkaline earths. When a hot saturated solution is cooled the base separates in the crystalline form with 8 molecules of water of crystallization. A solution of it is known as **baryta-water,** similar to "**lime-water.**" When a strong solution of sodium hydroxide is added to a strong solution of barium chloride a precipitate of barium hydroxide is formed. Unlike calcium and strontium hydroxides, barium hydroxide, when heated moderately, simply melts without forming the oxide.

692. Barium sulphate, $BaSO_4$. This compound, being extremely insoluble, may be readily prepared by adding a soluble sulphate to a solution of a barium salt. The finely divided white precipitate settles to the bottom of the vessel and may be freed from soluble impurities by stirring the precipitate repeatedly with pure water, allowing the precipitate to settle and pouring off the clear liquid. This process is called **washing by decantation.**

If barium sulphate be heated to a high temperature with charcoal it is reduced to barium sulphide:

$$BaSO_4 + 4 C = BaS + 4 CO.$$
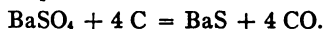
The product thus made treated with hydrochloric acid, gives **barium chloride** and hydrogen sulphide.

$$BaS + 2 HCl = BaCl_2 + H_2S.$$
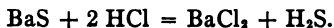
CHAPTER XLIII

RADIOACTIVITY AND RADIUM

693. Radioactivity. Certain substances emit continuously a peculiar invisible radiation which renders gases conductors of electricity, affects photographic plates, and produces fluorescence in certain solids. This activity is different from any known chemical action, in that it cannot be started or stopped, or its speed be increased or decreased by any known agency.

Becquerel first noticed in 1896 that uranium compounds all gave off these peculiar rays. In 1898 Madame Curie suspected that the enhanced radioactivity of pitchblende, a mineral containing uranium, was due to the presence of new elements. Working with over a ton of ore, she succeeded in isolating a few milligrams of a compound of a new element which she called radium.

694. Radium. In 1911 Madame Curie obtained the metal itself and found that it resembled barium. Its atomic weight has been found to be 226.5. Its compounds are extremely radioactive and are self-luminous. 1 g. of radium in combination gives off over 100 calories of heat per hour. This heat would be sufficient to raise the temperature of 1 g. of water from 0° to boiling, or more than enough to melt 1 g. of ice. More remarkable than this, however, is the fact that it spontaneously produces the gaseous element helium, at the rate of about 1 c.c of the gas for each gram of radium in eight years.

695. Kinds of rays. The rays coming from radioactive substances consist of three types, known respectively as alpha, beta, and gamma rays. **Alpha rays** consist of atoms of helium, carrying positive charges of electricity and capable of penetrating aluminum foil 1/20 mm. in thickness. **Beta rays** consist of very minute particles about 1/2000 as heavy as the

hydrogen atom, carrying negative charges of electricity, and, moving with a velocity almost equal to that of light (186,330 miles per second), are capable of penetrating aluminum foil 1 mm. in thickness. **Gamma rays** consist of electromagnetic waves capable of penetrating a lead plate many centimeters in thickness.

696. **Decomposition hypothesis.** The radioactivity of uranium compounds is proportional to the amount of uranium present. It is supposed that the atoms of all radioactive elements are made up of smaller particles in violent motion. These particles are being constantly thrown off with great velocity, giving rise to the formation of atoms of new radioactive elements. It thus appears that each radioactive element must have a limited duration of existence before it is completely transformed into other substances. The average lives of twenty or more of such elements have been approximately estimated and found to vary between five thousand million years and a fraction of a second.

697. **Uranium-radium series.**

Half-life period.

Uranium,   gives off alpha rays.........5,000,000,000 years.
  ↓

Uranium X, gives off beta and gamma
  ↓   rays...................24.6 days.

Ionium,   gives off alpha rays.........100,000 (?) years.
  ↓

Radium,   gives off alpha rays.........2,000 years.
  ↓

Niton,   gives off alpha rays.........3.86 days.
  ↓

Radium A, gives off alpha rays.........3.0 minutes.
  ↓

Radium B, gives off beta rays..........26.8 minutes.
  ↓

Radium C, gives off alpha, beta, and
  ↓   gamma rays..............19.5 minutes.

Radium D, gives off beta rays.........16.5 years.
   ↓

Radium E, gives off beta rays.........5.0 days.
   ↓

Radium F, gives off alpha rays........136.0 days.

Compounds of thorium and actinium give rise to other series similar to the uranium-radium series.

CHAPTER XLIV

MAGNESIUM, ZINC, CADMIUM, AND MERCURY

Magnesium (Laboratory Exercise No. 33)

698. Appearance and occurrence. Magnesium is a silver-white metal. The element does not occur in the metallic form but is abundantly found in compounds, especially as the carbonate, silicate, and chloride. Magnesium carbonate, or **magnesite**, $MgCO_3$, and **dolomite**, a double carbonate of magnesium and calcium, $MgCO_3CaCO_3$, are well known. It occurs as **kieserite**, $MgSO_4 \cdot H_2O$, and as **kainite**, $MgSO_4 \cdot KCl \cdot 6 H_2O$.

699. Physical properties. Magnesium is both malleable and ductile and is commonly furnished for the laboratory in the form of wire or ribbon. Its specific gravity is 1.75, it melts at 800°, and boils at 1100°.

700. Chemical properties. By far the most striking property of magnesium is the intense white light produced by the burning of the ribbon form.

The product of the combustion is magnesium oxide:

$$2 Mg + O_2 = 2 MgO.$$
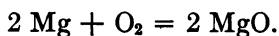
At a high temperature it unites with nitrogen to form magnesium nitride, Mg_3N_2. On account of its great attraction for oxygen it is a good reducing agent and will extract the oxygen from many oxides:

$$SiO_2 + 2 Mg = 2 MgO + Si.$$
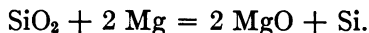
It dissolves easily in acids, usually with the liberation of hydrogen.

701. Test. In the presence of no other impurities than the salts of the alkali metals magnesium may be recognized by adding ammonium chloride, ammonium hydroxide, and sodium phosphate. The magnesium is thrown down as a finely di-

vided white crystalline precipitate of **ammonium magnesium phosphate**:

$$MgCl_2 + NH_4OH + HNa_2PO_4 = \underline{NH_4MgPO_4} + 2\ NaCl + \underline{HOH.}$$
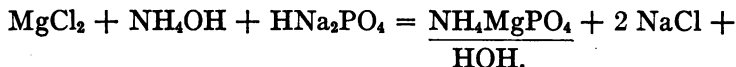
702. Preparation. The metal is prepared by the electrolysis of melted magnesium chloride, $MgCl_2$, or carnallite, $MgCl_2 \cdot KCl \cdot 6\ H_2O$, which has previously been dehydrated.

703. Uses. Magnesium is used in fireworks and mixed with potassium chlorate in **flash-light powders.**

704. Common compounds. Magnesium oxide, MgO; magnesium hydroxide, $Mg(OH)_2$; **magnesium sulphate**, or Epsom salt, $MgSO_4 \cdot 7\ H_2O$; **magnesium chloride**, $MgCl_2$; and magnesium carbonate, $MgCO_3$.

705. Magnesium oxide, or magnesia, MgO. This is the white powder which is formed when magnesium is burned, or is left as a residue when the carbonate is heated. It is a basic oxide with a slight alkaline reaction.

With water it forms magnesium hydroxide, which is a weak base and is very insoluble. The oxide unites with all acids, forming the corresponding magnesium salts.

706. Magnesium hydroxide, $Mg(OH)_2$, is precipitated from magnesium solutions by soluble hydroxides. It is very insoluble in water, but dissolves readily in solutions containing ammonium salts. This may be explained as follows: the undissociated magnesium hydroxide in saturated solution is in equilibrium with its ions:

$$Mg(OH)_2 \leftrightarrows Mg^{++} + OH^- + OH^-.$$
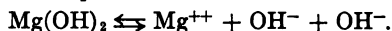
When a large amount of ammonium ions is introduced, some of the hydroxide ions combine with the ammonium to form ammonium hydroxide. This reduces the concentration of the hydroxide ions and more of magnesium hydroxide dissolves to restore the equilibrium. On account of the hydroxide ions constantly combining with the ammonium, it is impossible to completely restore the original equilibrium and so all of the magnesium hydroxide dissolves (249).

707. Magnesium chloride, $MgCl_2$. This is an extremely soluble and deliquescent salt. It may be made by the action of the metal, the oxide, or the carbonate on hydrochloric acid. When the solution is evaporated the basic salt, $Mg(OH)Cl$, and hydrochloric acid are formed. For this reason natural waters containing magnesium cannot be used in steam-boilers, for the hydrochloric acid set free would attack the iron.

708. Magnesium sulphate, Epsom salt, $MgSO_4 \cdot 7\ H_2O$, is much used in medicine and may be made by dissolving the metal, the oxide, or the carbonate in sulphuric acid.

709. Magnesium carbonate, $MgCO_3$, occurs in nature. When a soluble carbonate is added to a dissolved magnesium salt, the normal magnesium carbonate is not precipitated, but in place of it a basic carbonate having the composition shown by the formula, $Mg(OH)_2 \cdot 4\, MgCO_3 \cdot 4\, H_2O$, is thrown down. This compound is known to the druggist as **magnesia alba.**

Zinc

710. Appearance and occurrence. Zinc is a bluish-white crystalline metal. The commonest natural compounds of zinc are: **calamine,** $H_2Zn_2SiO_5$; **smithsonite,** $ZnCO_3$; **sphalerite,** ZnS; and **zincite,** ZnO. In the United States zinc ores are abundant in Missouri and New Jersey.

711. Physical properties. The metal has a specific gravity of 7–7.1, it melts at 419°, and boils at 918°. Cast zinc is brittle and the fracture shows a beautiful crystalline structure. Between the temperatures 120° and 150° it is malleable and ductile and may be rolled out into thin sheets. On cooling after such treatment it retains its malleability.

712. Chemical properties. When heated sufficiently it burns with a bluish-white flame, giving off dense white fumes of zinc oxide. Ordinary zinc displaces hydrogen from most acids, forming the corresponding salts:

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$
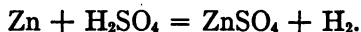
If, however, the zinc and acid are perfectly pure, there is little or no action. This is sometimes found to be the case in attempting to generate hydrogen from sulphuric acid and zinc. The action may be readily started by pouring a dilute solution of cupric sulphate over the zinc or adding it to the acid. Copper is deposited on the zinc, rendering it impure and setting up galvanic action.

713. Action of nitric acid. Strong nitric acid attacks zinc with violence, giving rise to the copious evolution of red fumes. The amount of reduction suffered by the acid varies with the concentration. For convenience the reaction with acid of specific gravity 1.2 may be represented by the equation:

$$3\, Zn + 8\, HNO_3 = 3\, Zn(NO_3)_2 + 2\, NO + 4\, H_2O.$$
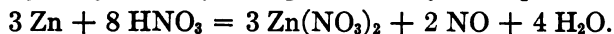
If the acid is very dilute it is reduced completely to ammonia, which unites with some of the acid, forming ammonium nitrate.

In order to reason out the equation for this case, it should be remembered that 1 atom of zinc would set free 2 hydrogen atoms from 2 molecules of nitric acid. To convert 1 molecule of nitric acid to ammonia would take 8 atoms of hydrogen from 8 molecules of the acid; the molecule of acid reduced, with 1 to convert the ammonia molecule to the nitrate, makes 10 molecules of nitric acid necessary. The original 8 atoms of hydrogen would be formed by 4 atoms of zinc; the equation would then be:

$$4 \, Zn + 10 \, HNO_3 = 4 \, Zn(NO_3)_2 + NH_4NO_3 + 3 \, H_2O.$$

714. Other reactions of zinc. Zinc displaces the hydrogen from hot alkalies, forming compounds known as **zincates**:

$$Zn + 2 \, NaOH = Na_2ZnO_2 + H_2.$$
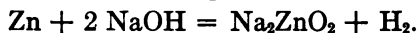
When ammonium sulphide is added to a solution of a zinc salt a white precipitate of zinc sulphide is formed:

$$(NH_4)_2S + ZnCl_2 = \underline{ZnS} + 2 \, NH_4Cl.$$
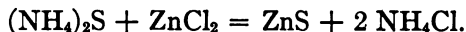
The sulphide is soluble in the common acids; therefore it cannot be completely precipitated from a neutral solution by hydrogen sulphide. The acid set free dissolves some of the precipitate:

$$ZnSO_4 + H_2S \leftrightarrows \underline{ZnS} + H_2SO_4.$$

The precipitate of zinc hydroxide first formed by the addition of sodium or potassium hydroxide to a solution of a zinc salt is redissolved by an excess of the alkali, forming a soluble **zincate.** That is, zinc hydroxide acts like a base toward strong acids, but like an acid toward strong bases:

$$Zn(OH)_2 + 2 \, HCl = ZnCl_2 + 2 \, HOH.$$
$$Zn(OH)_2, \text{ or } H_2ZnO_2 + 2 \, NaOH = Na_2ZnO_2 + 2 \, HOH.$$
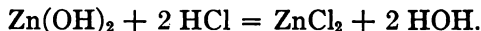
On account of its high solution pressure zinc displaces many other metals from solutions of their salts:

$$Zn + 2 \, AgNO_3 = 2 \, \underline{Ag} + Zn(NO_3)_2.$$
$$Zn + Cu(NO_3)_2 = \underline{Cu} + Zn(NO_3)_2.$$
$$Zn + SnCl_2 = \underline{Sn} + ZnCl_2.$$
$$Zn + Pb(NO_3)_2 = \underline{Pb} + Zn(NO_3)_2.$$
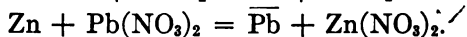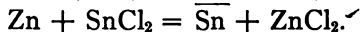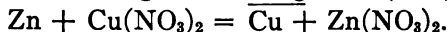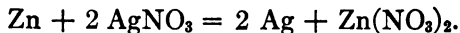
715. Test. Zinc solutions give a white precipitate of zinc sulphide on the addition of ammonium sulphide. Sodium hy-

droxide produces a white gelatinous precipitate which is readily dissolved by an excess of the reagent.

716. Preparation. (1) If an electric current be passed through a solution of a zinc salt, the metal separates in the crystalline form at the negative electrode.

(2) On the large scale the ore is first heated or roasted. In the case of carbonate the heating converts it to the oxide:

$$ZnCO_3 \text{ heated} = ZnO + CO_2.$$
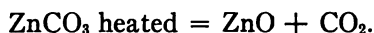
If the ore is a sulphide it is roasted. This converts the zinc to the oxide, and the sulphur passes off as sulphur dioxide:

$$2 ZnS + 3 O_2 = 2 ZnO + 2 SO_2.$$
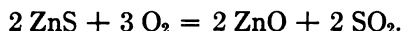
The zinc oxide is then mixed with carbon and heated in retorts. The zinc passes out of the retorts in the gaseous form and is condensed in earthenware receivers:

$$ZnO + C = Zn + CO.$$
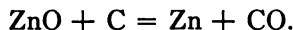
717. Uses. Brass contains from 20 to 40% zinc and from 80 to 60% copper. **Bronze** is brass with 3 to 10% of tin. **German silver** contains zinc 25%, nickel 25%, and copper 50%.

Galvanized iron is made by cleaning the iron thoroughly in acid and immersing it in molten zinc. This leaves the iron coated with a thin layer of zinc.

718. Common compounds. Zinc oxide, ZnO; **zinc chloride,** $ZnCl_2$; **zinc sulphate,** or **white vitriol,** $ZnSO_4 \cdot 7 H_2O$; **zinc carbonate,** $ZnCO_3$.

Zinc oxide. Zinc oxide may be made either by burning the metal or heating the carbonate. It is yellow when hot and white when cold. It is much used as a paint pigment.

Zinc chloride, $ZnCl_2$. This compound may be made by the action of hydrochloric acid on the metal, the oxide, or the carbonate, and may also be made by the direct union of the elements. It is extremely soluble and hygroscopic. Its water solution reacts acid and is much used by plumbers and tinsmiths as a soldering fluid. The tinsmith prepares his own soldering fluid by "cutting" zinc with muriatic acid.

Cadmium

719. Appearance and occurrence. Cadmium is a white metal resembling magnesium and zinc. It is found in small amounts associated with the ores of zinc, as the carbonate and sulphide. The mineral **greenockite,** CdS, is rare.

720. Properties. It is more malleable and ductile than zinc. It melts at 321° and boils at 778°. When heated sufficiently cadmium burns in air, giving off a brown smoke, which is cadmium oxide, CdO:

$$2\ Cd + O_2 = 2\ CdO.$$
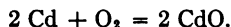
It sets hydrogen free from dilute acids, forming the corresponding salts, but is itself set free from solutions of its salts by zinc, which has a higher solution pressure.

Solutions of its salts when treated with hydrogen sulphide give a bright-yellow precipitate of the sulphide:

$$CdSO_4 + H_2S = \underline{CdS} + H_2SO_4.$$
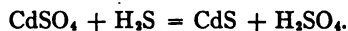
721. Test. With sodium hydroxide cadmium solutions give a white gelatinous precipitate insoluble in excess of the reagent, and with hydrogen sulphide a yellow precipitate.

722. Preparation. The metal may be prepared in the laboratory by placing a piece of zinc in a strong solution of cadmium sulphate:

$$Zn + CdSO_4 = \underline{Cd} + ZnSO_4.$$

It could also be prepared by heating cadmium oxide with charcoal in a porcelain tube to a temperature above the boiling-point of the metal:

$$CdO + C = CO + Cd.$$

723. Uses. The metal is used in the manufacture of certain alloys, especially **Wood's fusible metal,** and the sulphide is used as a yellow pigment.

724. Common compounds. Cadmium oxide, CdO; cadmium chloride, $CdCl_2 \cdot 2\ H_2O$; cadmium sulphate, $3\ CdSO_4 \cdot 8\ H_2O$; cadmium sulphide, CdS; cadmium nitrate, $Cd(NO_3)_2$.

Mercury

725. Appearance and occurrence. Mercury is· a silver-white metal which is liquid under ordinary conditions. It is found to some extent in the free condition, but chiefly as **cinnabar,** HgS, in Mexico and California.

726. Physical properties. The metal freezes at −39.5° and boils at 360°. It evaporates slowly at ordinary temperatures. Gold-leaf suspended over the surface of mercury in a bottle turns white in time. It has a specific gravity of 13.6. Vapor density determinations indicate that it contains only 1 atom in the molecule. It dissolves many other metals, forming alloys with them which may be either liquid or solid, and are known as **amalgams.** Pupils wearing gold or silver rings should

be warned not to handle mercury, as amalgamation and per-
haps ruin of the jewelry is bound to result.

727. Chemical properties.   Mercury does not tarnish in ordi-
nary air, but at higher temperatures it combines with oxygen
to form the oxide HgO, which at still higher temperatures
breaks up again into mercury and oxygen.   It unites directly
with the halogens, forming the corresponding halogen salts.   It
also unites directly with sulphur.

728. Action of nitric acid.   Dilute hydrochloric and sulphuric
acids do not attack it, and cold dilute nitric acid attacks it very
slowly at first, forming mercurous nitrate.   Hot dilute or the
cold concentrated nitric acid act with considerable violence and
produce a copious evolution of the red oxides of nitrogen.

The following equations may be used to represent these two
reactions:

Hot dilute nitric acid:

$$2 HNO_3 = H_2O + 2 NO + 3 O.$$
$$3 O + 3 Hg = 3 HgO.$$
$$\underline{3 HgO + 6 HNO_3 = 3 Hg(NO_3)_2 + 3 H_2O.}$$
$$3 Hg + 8 HNO_3 = 3 Hg(NO_3)_2 + 4 H_2O + 2 NO.$$

Concentrated nitric acid:

$$2 HNO_3 = H_2O + 2 NO_2 + O.$$
$$O + Hg = HgO.$$
$$\underline{HgO + 2 HNO_3 = Hg(NO_3)_2 + H_2O.}$$
$$Hg + 4 HNO_3 = Hg(NO_3)_2 + 2 NO_2 + 2 H_2O.$$
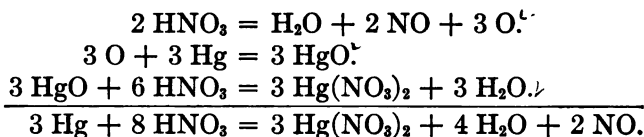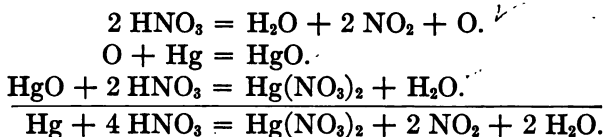
729. Other reactions.   Mercury forms two classes of com-
pounds: those in which the metal has a valence of 1, called
mercurous compounds; and those in which it has a valence of 2,
called **mercuric** compounds.

Zinc and copper both precipitate mercury from solutions of
its salts.   Hydrogen sulphide produces a black precipitate of
mercuric sulphide from all solutions of mercury salts.   In the
case of a mercurous salt the precipitate is mixed with a pre-
cipitate of mercury:

$$HgCl_2 + H_2S = HgS + 2 HCl.$$
$$2 HgNO_3 + H_2S = HgS + Hg + 2 HNO_3.$$
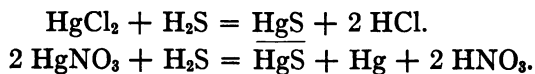
Sodium hydroxide added to a solution of a mercuric salt gives a yellow precipitate of mercuric oxide:

$$HgCl_2 + 2\ NaOH = Hg(OH)_2 + 2\ NaCl.$$
$$\underline{Hg(OH)_2 = HgO + H_2O.}$$
$$HgCl_2 + 2\ NaOH = \underline{HgO} + 2\ NaCl + H_2O.$$
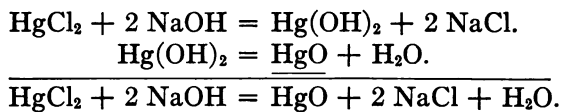
With a mercurous salt solution it gives a brown precipitate of mercurous oxide:

$$2\ HgNO_3 + 2\ NaOH = \underline{Hg_2O} + 2\ NaNO_3 + H_2O.$$

Stannous chloride solution added to a solution of mercuric chloride gives at first a white precipitate of mercurous chloride, which turns to a gray precipitate of metallic mercury on adding an excess of the reagent:

$$2\ HgCl_2 + SnCl_2 = \underline{Hg_2Cl_2} + SnCl_4.$$
$$Hg_2Cl_2 + SnCl_2 = \underline{2\ Hg} + SnCl_4.$$
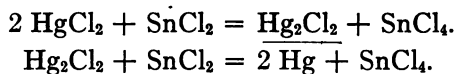
730. **Physiological properties.**   Mercury and all mercury compounds are poisonous, the more soluble the more poisonous. Finely divided mercury and insoluble mercury compounds, as well as strong solutions of mercury salts, coming too frequently in contact with the hands cause the skin to crack and bleed.

731. **Tests.**   If the solution silvers a piece of bright copper immersed in it, but does not give a white precipitate with hydrochloric acid, it contains mercury in the mercuric condition. If it contains the mercury in the mercurous condition, it will both silver a piece of bright copper and give a white precipitate with hydrochloric acid.

732. **Preparation.**   Mercury may be prepared in the laboratory by heating mercuric oxide in a sealed glass tube.   The oxygen passes out and the mercury condenses in the cold part of the tube:

$$2\ HgO\ \text{heated} \leftrightarrows 2\ Hg + O_2.$$
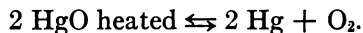
A piece of zinc or copper immersed in a mercury solution dissolves, and sets free an equivalent weight of mercury:

$$Zn + HgCl_2 = \underline{Hg} + ZnCl_2.$$
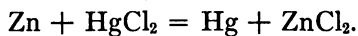
It is manufactured on the large scale by roasting the sulphide.

The sulphur passes off as sulphur dioxide, and the vapor of mercury is condensed in large chambers (Fig. 138).

733. Uses. Mercury is used in barometers, manometers, and thermometers. Sodium amalgam forms a valuable reducing
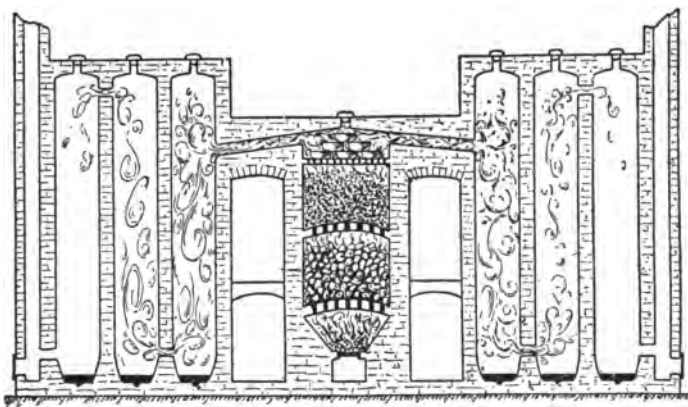
From Morgan and Lyman's "Chemistry, an Elementary Textbook," by permission of The Macmillan Company

FIG. 138

agent in the laboratory, and tin amalgam was formerly much used as a silver backing on mirrors.

Mercury is largely used in the extraction of gold and silver from their ores. The mercury forms amalgams with these metals, from which it may be driven off by heat and used again.

734. Common mercuric compounds. Mercuric oxide, red oxide of mercury, also called by the druggists **red precipitate,** HgO; mercuric chloride, **bichloride of mercury,** or **corrosive sublimate,** $HgCl_2$; mercuric nitrate, $Hg(NO_3)_2$; mercuric sulphide, natural form called **cinnabar,** artificial modification called **vermilion,** HgS.

Common mercurous compounds. Mercurous oxide, Hg_2O; **mercurous chloride,** or **calomel,** Hg_2Cl_2; mercurous nitrate, $HgNO_3$.

735. Mercuric chloride, $HgCl_2$, corrosive sublimate. Mercuric chloride may be made by dissolving mercuric oxide in hydrochloric acid, also by dissolving mercury in aqua regia. It is manufactured on the large scale by heating a mixture of mercuric sulphate with common salt. The mercuric chloride, being volatile, sublimes. The vapor of it is extremely poisonous and corrosive, hence the name "corrosive sublimate." 1 part of the salt will dissolve in 15 parts of water. A solution of 1 part in

1000–2000 parts of water is extensively used as an antiseptic in surgical operations.

736. Mercurous chloride, Hg_2Cl_2, or **calomel.** This compound of mercury may be prepared by adding a soluble chloride to a solution of a mercurous salt. It is prepared on the large scale, however, by subliming a mixture of mercuric chloride and mercury:

$$HgCl_2 + Hg = Hg_2Cl_2.$$
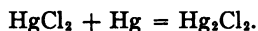
The substance is a fine white powder insoluble in water. When treated with ammonium hydroxide mercurous chloride turns black, on account of the formation of some finely divided metallic mercury. The following equation represents the reaction:

$$Hg_2Cl_2 + 2\,NH_4OH = HgClNH_2 + NH_4Cl + Hg + 2\,H_2O.$$

Mercurous chloride, in 1/10 to 2 grain tablets, is a very common household medicine.

737. Mercuric oxide, HgO. Mercuric oxide is a red crystalline powder when it is made by heating the metal in oxygen or air, but a yellow amorphous powder when it is made by adding an alkali to a solution of a mercuric salt. The oxide is basic and unites readily with acids to form the corresponding mercuric salts. When heated the oxide splits up into oxygen and mercury.

CHAPTER XLV

Copper and Silver

Copper (Laboratory Exercise No. 34)

738. Appearance and occurrence. Copper is a bright-red malleable and ductile metal. It is found in large quantities in the free condition in northern Michigan. It is found also very widely distributed in the form of various compounds, among which are **cuprite**, Cu_2O; **malachite** (a basic carbonate); **chalcocite**, Cu_2S; and **copper pyrites**, $CuFeS_2$.

739. Physical properties. Copper is very malleable and ductile, and may be beaten and rolled into thin sheets and drawn out into very fine wire. The specific gravity varies from 8.90 to 8.95. It melts at 1045°, boils at about 2100°, and forms alloys readily with zinc, nickel, tin, and aluminum.

740. Chemical properties. In dry air it remains bright, but in ordinary moist air it becomes covered with a thin coating of a basic carbonate which protects it from further action. When heated in the air it turns black, due to the formation of oxides of copper. If the hot metal be worked or bent, this black coating falls off in the form of thin scales, which when examined are black on the outside and red on the side which was next to the metal. This is due to the fact that there are two oxides of the metal. This material is called **copper scale.** The black oxide is called **cupric oxide,** CuO, and the red, **cuprous oxide,** Cu_2O. Copper forms two classes of compounds analogous to those formed by mercury. Those in which the metal apparently has a valence of 1 are called **cuprous compounds** and those in which it has a valence of 2 are called **cupric compounds.**

741. Action of nitric acid. Both concentrated and dilute nitric acid attack the metal with considerable violence, giving off the red oxides of nitrogen.

For the concentrated acid the following equation represents the action:

$$2\ HNO_3 = H_2O + 2\ NO_2 + O.$$
$$O + Cu = CuO.$$
$$\underline{CuO + 2\ HNO_3 = Cu(NO_3)_2 + H_2O.}$$
$$Cu + 4\ HNO_3 = Cu(NO_3)_2 + 2\ H_2O + 2\ NO_2.$$
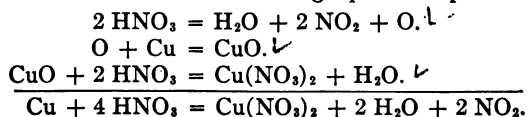
For the dilute acid it should be remembered that nitric oxide, NO, is one of the products, and that this results from the reduction of 2 molecules of nitric acid by the loss of 3 atoms of oxygen. These 3 atoms of oxygen form 3 molecules of cupric oxide, which in turn combine with 6 molecules of nitric acid, making 8 molecules of the acid necessary for the reaction. The equation may now be written directly:

$$3\,Cu + 8\,HNO_3 = 3\,Cu(NO_3)_2 + 2\,NO + 4\,H_2O.$$
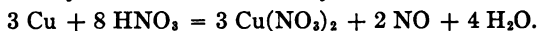
742. Other reactions. Cold dilute sulphuric and hydrochloric acid have no effect upon it, but hot concentrated sulphuric acid attacks it, with the formation of anhydrous copper sulphate and sulphur dioxide:

$$H_2SO_4 = H_2O + SO_2 + O.$$
$$O + Cu = CuO.$$
$$\underline{CuO + H_2SO_4 = CuSO_4 + H_2O.}$$
$$Cu + 2\,H_2SO_4 = CuSO_4 + 2\,H_2O + SO_2.$$
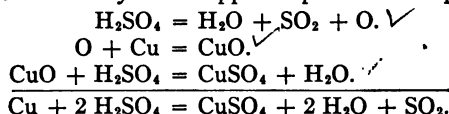
The metal unites directly also with the halogens and sulphur.

Copper precipitates silver and mercury from solutions of their salts and is itself thrown out of solution by magnesium, zinc, iron, or aluminum (196).

When hydrogen sulphide is passed through a solution of a copper salt all of the copper is precipitated as black cupric sulphide, which is insoluble in dilute acids:

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$
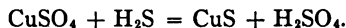
If sodium or potassium hydroxide be added to a solution of a cupric salt, a light-blue gelatinous precipitate of cupric hydroxide is thrown down. If the solution containing this precipitate be heated, the cupric hydroxide loses water and is converted to cupric oxide:

$$CuSO_4 + 2\,NaOH = Cu(OH)_2 + Na_2SO_4.$$
$$Cu(OH)_2 \text{ heated} = CuO + H_2O.$$
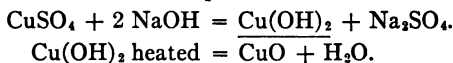
The oxide is precipitated at once if the alkali be added to the hot copper solution.

If a cupric sulphate solution to which some grape-sugar has been added be made strongly alkaline with sodium hydroxide and heated, the copper sulphate is reduced to **cuprous oxide**, Cu_2O, which appears as a red precipitate.

All cupric solutions are blue, but, if an excess of ammonium hydroxide be added, a much deeper blue solution is formed. When the ammonium hydroxide is first added a light-blue precipitate of cupric hydroxide is formed, which immediately dissolves in an excess of ammonia. This is due to the formation of a soluble compound of ammonia with the copper salt.

743. Tests. With ammonium hydroxide a deep-blue solution is formed. Hydrogen sulphide gives a black precipitate. Bright iron wire immersed in a copper solution becomes cov-

ered with copper. The solution boiled with sodium hydroxide gives a black precipitate of cupric oxide.

744. Preparation. (1) Metallic copper may be easily prepared in the laboratory by passing an electric current through a solution of a copper salt. The metal is deposited on the negative electrode.

(2) It may also be prepared by heating copper oxide with a reducing agent:

$$CuO + C = Cu + CO.$$
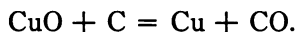
(3) Illuminating gas or hydrogen passed over red-hot copper oxide reduces it to the metal:

$$CuO + H_2 = Cu + H_2O.$$
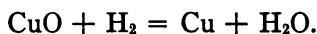
(4) **The extraction of copper from its ores,** on the large scale, is a rather complicated process if much sulphur is present. Ores containing little sulphur are simply heated with carbon and sufficient fluxing material to combine with the sand and other impurities present. The melted copper is run off from the bottom of the furnace.

FIG. 139

When much sulphur is present the ores are broken up and roasted, to convert some of the sulphides to oxides. The whole is then melted with sand, to convert the iron to silicate, which is run off with the slag. The product from this melting contains about 50 per cent copper mixed with iron and sulphur and is called **matte.** The matte is run into converters lined with sand (Fig. 139). A blast of air is then introduced below the surface of the liquid contents. The sulphur is converted to sulphur dioxide, and the iron combines with the lining of the converter, forming a liquid slag. After the action is over the slag is first run off and the melted copper cast into plates known as **anodes,** of a form convenient for electrolytic refining.
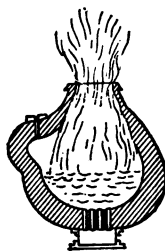
FIG. 140

745. Electrolytic refining. Copper obtained by the above method is not perfectly pure and is further purified by means of the electric current. For this purpose the copper anodes, which have been cast in the proper form, are suspended in large vats filled with a solution containing 15 per cent of blue vitriol and 5 per cent of sulphuric acid. Between the anodes and very close to them thin sheets of pure copper, called **cathodes,** are suspended
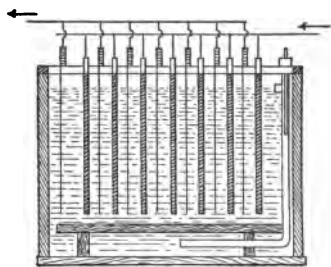
(Fig. 140). All of the anodes are connected with the positive terminal of a generator and all of the cathodes with the negative. Copper ions enter the solution from the anodes while an equal number of copper ions from the solution are deposited as pure copper on the cathode. In this way the cathodes slowly grow until they weigh over 200 lbs. All of the impurities from the anodes accumulate in the bottom of the tank in the form of mud. This mud is ultimately refined and much gold and silver recovered.

746. Uses. The uses of copper are so numerous that it is impossible to mention them all. On account of its high conductivity, copper wire is universally used in all electrical installations. Sheet copper is used in roofing, for sheathing of wooden and iron ships, and for the construction of all manner of cooking utensils. It is also used in **electrotyping.** For this purpose, after the ordinary type has been set, an imprint of the type is made in wax, the surface of the wax is coated with a thin layer of graphite to render it a conductor, and it is immersed in a copper sulphate solution and plated with copper. In this way a thin sheet of copper is obtained which is an exact duplicate of the type. To render it stronger it is backed with type metal and is ready at once for the press.

747. Alloys. Besides its use in the pure condition, copper constitutes an important ingredient of many alloys, some of which, with their approximate compositions, are as follows:

Brass, copper 60–80%, zinc 40–20%.
Bronze, copper 80–90%, tin 5–10%, zinc 0–10%.
Aluminum bronze, copper 90%, aluminum 10%.
German silver, copper 50%, nickel 25%, zinc 25%.
Gold coin, copper 10%, gold 90%.
Silver coin, copper 10%, silver 90%.
Nickel coin, copper 65%, nickel 35%.

748. Common compounds. Cuprous oxide, or red oxide of copper, Cu_2O; **cuprous chloride,** Cu_2Cl_2; **cupric oxide,** or black oxide of copper, CuO; **cupric chloride,** $CuCl_2$; **cupric sulphate,** or blue vitriol, $CuSO_4 \cdot 5\ H_2O$; **cupric nitrate,** $Cu(NO_3)_2$; **cupric sulphide,** CuS.

749. Cuprous oxide, Cu_2O. If a solution of cupric sulphate containing some grape-sugar and made strongly alkaline with sodium hydroxide,

be heated, a red precipitate of cuprous oxide will be obtained. This oxide may also be prepared by adding sodium hydroxide to a hot solution of cuprous chloride in hydrochloric acid.

750. Cuprous chloride, Cu_2Cl_2. If a solution of cupric chloride, made strongly acid with HCl, be boiled with a large quantity of copper wire until it becomes almost clear and then be poured into an excess of water, a heavy white precipitate of cuprous chloride will be formed. The cuprous chloride is insoluble in water. If it is left in contact with the air while moist, it rapidly turns green.

751. Cupric oxide, or black oxide of copper, CuO. When copper is heated in oxygen it is converted to the oxide, CuO. Cupric oxide may also be prepared by heating the nitrate or the carbonate. In the "wet way" it may be made by adding sodium hydroxide to a hot solution of a cupric salt.

752. Cupric sulphate, or blue vitriol, $CuSO_4 \cdot$ $5 H_2O$. This is the well-known compound used in gravity batteries. It also goes by the name "bluestone." It is obtained as a by-product in the refining of gold and silver, and may also be made by dissolving copper in hot concentrated sulphuric acid. This reaction gives the anhydrous salt which is without color and only turns blue on the addition of water. In ordinary air the crystallized salt shows little tendency to effloresce, but if it be placed in a draft it effloresces appreciably. At 100° it loses 4 molecules of water. It crystallizes in the tri-clinic system (Fig. 141).
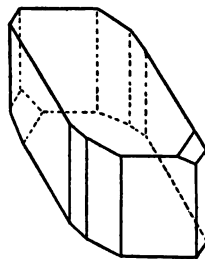
Fig. 141

753. Sulphides of copper. If hydrogen sulphide be passed through a solution of a cupric salt, a black precipitate of cupric sulphide is formed. If the metal be heated in the vapor of sulphur, cuprous sulphide, Cu_2S, is formed.

Silver

754. Appearance and occurrence. Silver is a perfectly white metal. It occurs in the free condition, sometimes in very large masses, but is chiefly found as the sulphide and chloride. The chloride is known as **horn-silver.** The Rocky Mountain section of America is the greatest silver-producing region in the world. Much silver is obtained as a by-product in the refining of lead, copper, and gold.

755. Physical properties. The metal crystallizes in perfect octahedrons, melts at 954°, has a specific gravity of 10.5, and is the best conductor of heat and electricity. The melted metal absorbs a great quantity of oxygen, which is spurted out again during solidification. The

metal is extremely malleable and ductile and may be rolled and hammered out into thin sheets and drawn out into very fine wire.

756. Chemical properties. Silver does not combine with oxygen under ordinary pressure, and the oxides of silver when heated give up the oxygen. Several oxides are known: Ag_2O (silver oxide), Ag_2O_2 (silver peroxide), and Ag_4O (silver suboxide).

Silver is not attacked by hydrochloric or cold sulphuric acid. Hot concentrated sulphuric acid converts it to the sulphate with the liberation of sulphur dioxide:

$$2\ Ag + 2\ H_2SO_4 = Ag_2SO_4 + 2\ H_2O + SO_2.$$

It is also readily dissolved by dilute nitric acid with the evolution of nitric oxide. It will be remembered that 2 molecules of nitric acid decompose to form 3 atoms of oxygen, which are equivalent to 6 atoms of silver. These require 6 molecules more of the acid to convert them to the nitrate; therefore the equation may be written at once:

$$6\ Ag + 8\ HNO_3 = 6\ AgNO_3 + 2\ NO + 4\ H_2O.$$

A soluble chloride added to a solution of a silver salt gives a white, curdy reprecipitate of silver chloride, soluble in ammonium hydroxide and insoluble in nitric acid. Addition of nitric acid to the ammonia solution reprecipitates the chloride.

Mercurous mercury compounds, as well as lead compounds, also give white precipitates with soluble chlorides which are insoluble in nitric acid; but the mercurous chloride is turned black by ammonia and the lead chloride is soluble in hot water.

All silver compounds are blackened by sunlight, especially the chloride, bromide, and iodide. Although bright silver does not oxidize in the air, it is extremely sensitive to sulphur, and minute traces of the element or of hydrogen sulphide in 'the air, cause the surface to blacken. Silver spoons are blackened by the sulphur in eggs. So-called "oxidized silver" is made by dipping the object into a solution of potassium sulphide.

Silver is thrown out of solution by copper, zinc, and mercury:

$$2\ AgNO_3 + Cu = \underline{2\ Ag} + Cu(NO_3)_2.$$
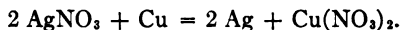
Hydrogen sulphide produces a black precipitate of **silver sulphide** when passed into a solution of silver. Potassium chromate or dichromate produces a deep-red precipitate of **silver chromate** in neutral solutions of silver salts.

757. Test. Solutions of silver compounds give a white, curdy precipitate of the chloride insoluble in nitric acid and soluble in ammonium hydroxide when hydrochloric acid or a soluble chloride is added.

Also when a clean copper wire is placed in a solution of a

silver compound crystalline metallic silver collects about the wire.

758. Preparation. When the electric current is passed through a silver solution the metal separates in the crystalline form on the negative electrode. The nitrate and carbonate are reduced to metallic silver by simply heating to a high temperature. The chloride, bromide, or iodide may be converted to the metal by being left in contact with moist granulated zinc, or by melting with an excess of sodium carbonate in a sand crucible. If it is desirable to separate silver from an alloy containing copper the alloy is dissolved in the least possible quantity of nitric acid, and an excess of copper wire placed in the solution. All of the silver is thrown out of solution and an equivalent amount of copper is converted to the nitrate.

759. The reduction of silver from its ores. Many different processes are used in obtaining silver from its ores. If the ore is essentially a silver ore and does not contain much copper or lead, it is roasted with salt to convert the silver to the chloride. This is then reduced with iron:

$$2\,AgCl + Fe = FeCl_2 + 2\,Ag.$$
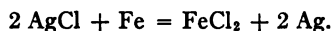
Lead ores frequently carry a small amount of silver. The ore is smelted for the lead and the silver extracted from the latter by **Parke's** process. This process is based on the fact that silver dissolves in melted zinc, while the latter does not alloy appreciably with the lead. The melted lead, carrying a small amount of silver, is violently agitated with a small amount of melted zinc. The silver leaves the lead and forms an alloy with the zinc which floats on the surface of the lead and may be skimmed off. The silver is recovered by distilling off the zinc. Much silver as well as gold is obtained from the mud which settles to the bottoms of the tanks in the electrolytic purification of copper.

760. Refining silver. Silver obtained by the above processes is impure and is refined by dissolving it in hot concentrated sulphuric acid. This converts all of the metals present, except gold, to the corresponding sulphates. The gold is left in the metallic form and recovered. The solution of the sulphates is diluted and treated with metallic copper. The copper goes into solution as copper sulphate and the silver is set free.

761. Uses. Silver is used for ornaments, tableware, for plating other metals, and for coinage. Pure silver is very soft and is frequently alloyed with a small amount of copper to give it hardness and strength. The **silver coinage** of the United States contains 10 per cent of copper. An alloy containing 92.5 per cent is called **sterling silver.**

762. Silver-plating. Objects to be silver-plated are suspended in a solution made by adding potassium cyanide to a silver nitrate solution

until the precipitate of silver cyanide which forms at first is entirely redissolved. The objects are connected with the negative terminal of a generator and form the **cathode,** or negative electrode. The **anode,** or positive electrode, is a sheet of silver which is connected with the positive terminal. When the current is turned on, ions of silver enter the solution from the silver plate and an equivalent number of silver ions from the solution move over to the objects, where they give up their positive charges and appear in the free condition as a coating of silver (Fig. 142).
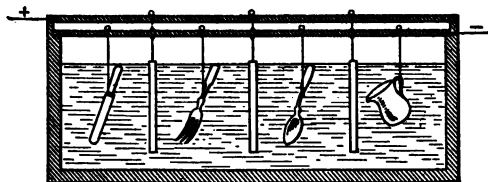
FIG. 142

763. Mirrors. In the manufacture of mirrors two solutions are prepared. The silver solution is made by adding ammonium hydroxide to a silver nitrate solution until the precipitate formed at first is just redissolved. The second solution contains the reducing agent. Many different substances may be used as reducing agents. Examples of such substances are: ammonium tartrate, formaldehyde, acetaldehyde, and cane-sugar, to which a small quantity of nitric acid has been added.

The glass to be silvered, after having been thoroughly cleaned, is laid in a horizontal position on a table which admits of being warmed by steam. The silver and reducing solutions are mixed just before being used and poured over the glass plate. If necessary, the plate is slightly warmed. All of the silver is deposited on the glass in about fifteen or twenty minutes. The coating is washed, dried, and varnished. Bright copper or brass objects may be readily silvered by rubbing them with a paste made by adding silver nitrate solution to dry powdered sodium sulphite.

764. Common compounds. Silver nitrate, or lunar caustic, $AgNO_3$; silver chloride, $AgCl$; silver bromide, $AgBr$; silver iodide, AgI; silver sulphite, Ag_2SO_3.

765. Silver nitrate, $AgNO_3$. The commonest compound of silver in the laboratory is silver nitrate. It is a colorless crystalline solid made by dissolving the metal in nitric acid. It melts at low temperatures without decomposing, and in the form of sticks is sold in the drug-stores as **lunar caustic.**

Solutions of this salt produce black spots on the skin and on cloth when exposed to light. For this reason silver nitrate forms one of the ingredients of **indelible ink,** used in marking linen.

766. Photography. Photographic processes depend on the fact that the halogen salts of silver are affected by light in a

peculiar way proportional to its intensity. The halogen salts are all blackened when exposed to direct sunlight for a long time, but if the bromide is exposed even for a fraction of a second it is affected in such a way that when treated with certain reducing solutions known as **developers,** a black deposit of silver is obtained. The intensity of this color is proportional to the intensity of the light striking the bromide.

The various operations involved in the ordinary photographic process may be considered under the following heads:

1. Preparation of the emulsion containing the sensitive silver salt.

2. Preparation of the plate or film.

3. The exposure.

4. The development of the negative.

5. The treatment of the plate with sodium thiosulphate ($Na_2S_2O_3$), commonly called **hypo.** This process is called **fixing.**

6. Printing.

7. The development and "fixing" of the picture or positive.

767. Preparation of the emulsion. A solution of gelatine or collodion is treated with silver nitrate, and enough ammonium bromide to convert all of the silver to the bromide. The emulsion is dried and washed with water to remove all of the ammonium nitrate. It is then melted or dissolved and is ready to be applied to the plate or film.

768. Preparation of the plate or film. The glass plate or film is thinly coated on one side with the melted or dissolved emulsion prepared as above. The plates or films are allowed to harden or dry in a room protected from light and when dry are ready for use in the camera.

769. The exposure. When the plate has been placed in the camera and the focus adjusted so that a perfect image of the object will fall on the plate, the exposure is made either by snapping the shutter or removing the cap. The time of exposure varies with the intensity of the light. After the exposure, when the plate is examined in the dark room, no trace of the picture can be seen until after development.

770. The development. When the plate was exposed the light changed the silver bromide to silver subbromide in varying

amounts according to its intensity. When the plate is treated with a reducing solution metallic silver is set free and the picture becomes visible on a light-colored background of unchanged silver bromide. This plate could not be exposed to light, for the unchanged silver salt would be darkened. It is therefore necessary to remove all of the unaltered silver compound remaining on the plate.

771. Fixing. The plate is now soaked for some time in a solution of sodium thiosulphate (hyposulphite of soda), which dissolves all of the unchanged silver bromide. After washing and drying, the plate is ready to be used in printing the picture on sensitive paper.

772. Printing. In printing, the negative is clamped in a printing-frame with the image side next to the sensitive side of the prepared paper.

If the paper is a silver bromide paper a very short exposure is necessary and the image does not appear until it is developed as in the case of the negative. If it is a silver chloride paper a long exposure is necessary and the picture slowly appears and need only be treated with "hypo" when sufficiently clear. The pictures, after development and fixing, are washed thoroughly to remove all traces of the "hypo," and after drying are ready for mounting.

CHAPTER XLVI

MANGANESE

(Laboratory Exercise No. 35)

773. Appearance and occurrence. Manganese is a metal resembling iron in appearance. It does not occur in the free condition, but is found very widely distributed as the mineral **pyrolusite, or black oxide of manganese,** MnO_2, otherwise known as manganese dioxide. The pupil is already familiar with this substance as the black powder which is used mixed with potassium chlorate in the preparation of oxygen and with hydrochloric acid in the preparation of chlorine.

774. Physical and chemical properties. The metal has a brilliant lustre, is very hard, has a specific gravity of 7.7, and melts at about 1245° C. The formulas of the various compounds of manganese indicate that the element has valences of 2, 3, 4, 6, and 7. Six oxides are known: MnO, manganous oxide; Mn_2O_3, manganic oxide; MnO_2, manganese dioxide; Mn_3O_4, manganous-manganic oxide, similar in composition to magnetic oxide of iron; MnO_3, manganese trioxide, or manganic anhydride; Mn_2O_7, manganese heptoxide, or permanganic anhydride. All but the last two of the above oxides are stable and well known; the others are not easily prepared.

In general, the lower oxides of manganese are basic and the higher acidic. MnO, **manganous oxide,** unites with acids with the formation of manganous salts:

$$MnO + 2\ HCl = MnCl_2 + H_2O.$$
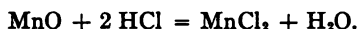
Mn_2O_3, **manganic oxide,** is the basic oxide contained in a few manganic salts.

MnO_3, **manganese trioxide,** is the anhydride of manganic acid, H_2MnO_4.

All manganese compounds, when melted with sodium carbonate and an oxidizing agent, such as potassium chlorate or nitrate, are converted to potassium manganate, K_2MnO_4, which is green in color.

If a solution of potassium manganate be acted upon by an acid, it is converted to potassium permanganate, $KMnO_4$.

The permanganate ion MnO_4^- produces a deep-purple color in solution:

$$3\ K_2MnO_4 + 4\ HNO_3 = 2\ KMnO_4 + MnO_2 + 4\ KNO_3 + 2\ H_2O.$$

This change may also be brought about by simply boiling the solution.

Potassium permanganate, $KMnO_4$, is a powerful oxidizing agent, 2 molecules giving 5 atoms of available oxygen in acid solution:

$$2\ KMnO_4 = K_2O + 2\ MnO + 5\ O.$$
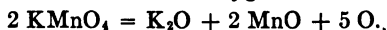
The acid that is either present or formed combines with the basic oxides,

437

converting them to the corresponding salts. When just sufficient reducing agent has been added to combine with all of the oxygen the purple color entirely disappears:

$$2 \ KMnO_4 = K_2O + 2 \ MnO + 5 \ O.$$
$$5 \ O + 5 \ H_2SO_3 = 5 \ H_2SO_4.$$
$$K_2O + H_2SO_4 = K_2SO_4 + H_2O.$$
$$\underline{2 \ MnO + 2 \ H_2SO_4 = 2 \ MnSO_4 + 2 \ H_2O.}$$
$$2 \ KMnO_4 + 5 \ H_2SO_3 = K_2SO_4 + 2 \ MnSO_4 + 3 \ H_2O + 2 \ H_2SO_4.$$
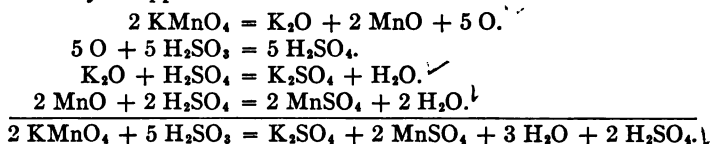
Manganese metal itself dissolves in acids, with the liberation of hydrogen and the formation of manganous salts:

$$Mn + 2 \ HCl = MnCl_2 + H_2.$$
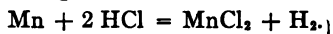
775. Tests. Manganous solutions, added with much stirring to an ammoniacal solution of a phosphate, form a brilliant pink, pearly, crystalline precipitate of ammonium manganese phosphate:

$$NH_4OH + MnCl_2 + HNa_2PO_4 = \underline{NH_4MnPO_4} + 2 \ NaCl + HOH.$$
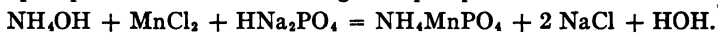
If a small amount of a solid containing manganese be fused on platinum foil with sodium carbonate and a little potassium nitrate, a green color will be formed.

If a compound of manganese be dissolved in boiling dilute nitric acid and a little red lead added, the manganese is changed to permanganic acid, which is recognized by the purple color after the oxide of lead has settled.

776. Preparation. Manganese might be made by the reduction of the oxide with carbon at a high temperature:

$$Mn_3O_4 + 4 \ C = 3 \ Mn + 4 \ CO.$$
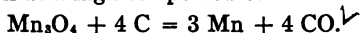
The metal may be easily made in the laboratory by **Goldschmidt's reaction.** In this reaction an oxide of the metal is mixed with the theoretical amount of powdered aluminum in a large crucible and the mixture ignited. A violent reaction ensues with the evolution of an intense heat. The oxygen of the manganese dioxide goes over to the aluminum, forming aluminum oxide, and the manganese settles to the bottom of the crucible in the liquid condition:

$$Mn_2O_3 + 2 \ Al = Al_2O_3 + 2 \ Mn.$$
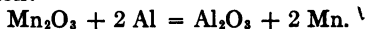
This reaction can also be used for the preparation of several other metals.

777. Uses. Manganese is seldom prepared in the pure form except as a laboratory curiosity. An alloy of iron and manganese known as **spiegeleisen** is used extensively in the manufacture of steel. Manganese dioxide is used in dry batteries as a depolarizer, and potassium permanganate is used as an oxidizing agent and disinfectant.

778. Common compounds. Manganese dioxide, MnO_2; manganous sulphate, $MnSO_4$; potassium permanganate, $KMnO_4$.

Manganese dioxide, MnO_2. This compound, as it is ordinarily used in the laboratory, consists of the pulverized or granulated mineral **pyrolusite.** It is of importance in the manufacture of chlorine:

$$MnO_2 + 4\,HCl = MnCl_2 + 2\,H_2O + Cl_2.$$

It is also used as a catalytic agent with potassium chlorate in the preparation of oxygen. It causes the oxygen to be set free from the chlorate at a low temperature.

It is insoluble in nitric acid and virtually so in cold dilute sulphuric, but if a reducing agent be added to the acid it dissolves almost instantly.

Vessels blackened with the dioxide may be readily cleaned by washing with a solution of sulphur dioxide.

When heated, manganese dioxide changes to the red oxide Mn_3O_4, with the evolution of oxygen:

$$3\,MnO_2 \text{ heated } = Mn_3O_4 + O_2.$$
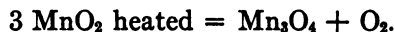
CHAPTER XLVII

IRON

(Laboratory Exercise No. 35)

779. Appearance and occurrence. Iron is a white metal with a brilliant lustre. It occurs in the free condition in minute quantities in certain volcanic rocks and also in meteorites. The common ores of iron are the oxides, **hæmatite**, Fe_2O_3, and **magnetite**, Fe_3O_4, and the carbonate, $FeCO_3$, also known as **siderite**. Iron is also present in nearly all rocks, in the soil, and in all vegetable and animal matter.

780. Three kinds of iron. Pure iron is almost a chemical curiosity. The commercial forms of iron may be divided into three classes: **cast iron, wrought iron,** and **steel**. The properties of these three kinds of iron vary according to the mode of manufacture and the varying quantities of certain impurities. The impurities present in almost all forms of iron and steel are the following: **carbon, silicon, sulphur, phosphorus,** and **manganese.** These are necessarily present, for the reason that they are always present in the iron ore and coke used in the primary reduction of the ore. Other elements either present in the iron or introduced for the purpose of giving the product particular properties are: oxygen, nitrogen, copper, aluminum, titanium, nickel, chromium, vanadium, tungsten, and molybdenum.

781. Table showing the approximate proportions of impurities in the common forms of iron and steel:

		Carbon	Silicon	Sulphur	Phosphorus	Manganese
Iron	Pig-Iron.........	2.6–6.3%	2.5–4%	.01–.1%	.1–1%	.1–1.5%
	Cast iron........	2.5–4%	2.5–4%	.01–.1% .	.1–1%	.10–1.5%
	Spiegel-iron.......	4–5%	.3–3%	.01–.08%	.05–.15%	5–20%
	Wrought iron......	.1–.2%	.0–.3%	.0–.1%	.1–.2%	.1–1.5%
Steel	Low steel.........	.08–.15%	.05–.1%	.01–.06%	.05–.1%	.1–.5%
	Railroad-iron......	.35–.45%	.05–.1%	.01–.06%	.05–.1%	.6–1%
	Tool-steel.........	.5–1.5%	.002–.07%	.005–.015%	.002–.015%	.0–.5%

782. Pig-iron is iron just as it comes from the blast-furnace. It contains much free carbon in the form of graphite. It is neither malleable nor ductile.

783. Cast iron is usually made by melting pig-iron in a suitable furnace and pouring the melted iron into sand moulds. It is very brittle and cannot be used for articles that are to be subjected to great tensile or bending strain. The fracture is gray, and, although the grain is much finer than that of pig-iron, this variety also contains free carbon in the form of graphite. If the cast iron is cooled suddenly, the carbon remains in combination with the iron, producing a variety which is extremely hard and brittle, known as **chilled iron.**

784. Spiegel-iron is a variety of cast iron very rich in carbon, silicon, and manganese, which is used in the manufacture of steel. It gets its name from the fact that its fracture is very white and brilliant.

785. Wrought iron is very nearly pure iron. It is malleable and ductile, and may be drawn out into fine wire and rolled into thin sheets. It is made by melting pig-iron with iron ore in a furnace known as a **puddling-furnace.** The ore acts as an oxidizing agent burning out the impurities from the iron. As the temperature of the furnace is not high enough to melt the resulting wrought iron, the latter collects as a pasty mass and is removed from the furnace in large balls dripping with slag. These masses, known as **puddle-balls,** after a preliminary squeezing to remove excess of slag, are rolled into finished bars of various shapes.

The presence of slag in the ball results in fine streaks of slag in the finished rolled iron, giving it the appearance of a grain.

786. Steel. By the term "steel" was formerly meant iron containing enough carbon to cause it to harden when suddenly cooled. To-day the term means any product turned out by the Bessemer converter, the open-hearth process, or the crucible process. For convenience, we may distinguish between low steel, or structural iron, and high steels.

Low steel, or structural iron, containing from .08% to .15% carbon, is similar to wrought iron except that it does not have streaks of slag. It is very malleable and ductile and may be

rolled into all sorts of shapes. It is used in the construction of roofs, bridges, and buildings. It is made by either the Bessemer or open-hearth process.

Railroad-iron contains from .35% to .55% carbon and from .6% to 1% manganese. It is also made by either the Bessemer or open-hearth process.

High steel, or tool-steel, contains from .5% to· 1.5% carbon as the chief ingredient in addition to the iron. As a result of this high percentage of carbon,· it is possible to harden it by sudden cooling. This process is called tempering. The hardness attained depends upon the temperature of the steel at the time it is plunged into the water. Tools are tempered according to the work they are intended to perform. Iron-cutting tools are made much harder than tools designed for wood-working.

If this kind of steel be heated and allowed to cool slowly, it remains almost as soft as low steel or wrought iron.

787. Metallurgy of iron. Iron ore is reduced to iron in a large cylindrical furnace known as a **blast-furnace.** The whole structure is from 90 to 100 ft. high, 20 to 25 ft. in diameter inside, at the widest part, and narrower at both top and bottom (Fig. 143). At the bottom, just above the surface of molten iron and slag, a set of blast-pipes, called **tuyeres,**
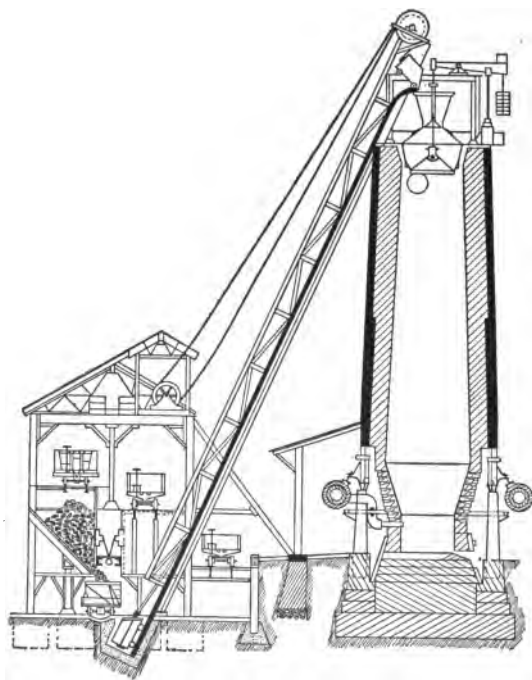
Fig. 143

enter the furnace. When the furnace is in operation a blast of hot air is blown in through these tuyeres.

When the furnace is once started alternate layers of coke, iron ore, and lime or limestone are periodically charged in at the top. The lime or limestone is used when the ore contains much sand. It unites with the sand, forming a fusible slag. In case the ore were rich in basic materials, such as lime or magnesia, it would be necessary to add sand in place of lime. The reactions are about as follows:

(1) The coke burns to carbon dioxide:

$$C + O_2 = CO_2.$$
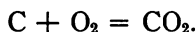
(2) The carbon dioxide in contact with hot carbon is reduced to carbon monoxide:

$$CO_2 + C = 2\ CO.$$
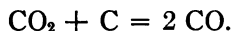
(3) The carbon monoxide extracts oxygen from the iron ore, becoming again carbon dioxide:

$$Fe_2O_3 + 3\ CO = 2\ Fe + 3\ CO_2.$$
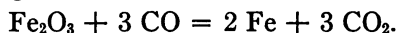
The iron is formed in minute globules and rapidly settles to the bottom of the furnace. The molten slag, containing all of the sand, lime, and mineral impurities of the ore, collects on top of the iron and must be drawn off from time to time. The furnace is tapped three or four times in every twenty-four hours and the iron is run off into moulds, forming **pig-iron,** or directly into ladles and carried to the steel-making plant without being allowed to harden. When the process is once started it may run for years without stopping. Since the iron ore itself always contains silicon, sulphur, phosphorus, and manganese it is easily understood why these elements are always found in the resulting product. The carbon, of course, comes from the coke.

788. Metallurgy of steel. Steel is made from pig-iron, or from the melted iron directly from the blast-furnace, by oxidizing just the right quantity of carbon. This is accomplished by several different processes. In the **open-hearth process** the pig iron is heated in a reverberatory furnace in contact with iron ore. The oxygen of the ore oxidizes the carbon of the iron. In the **Bessemer process** a blast of air is blown through the

melted iron, which burns out all of the carbon together with some of the other impurities, and then a definite amount of iron rich in carbon is added to return the proper quantity of carbon to the product.   In the crucible process a very pure wrought iron is melted in pots with just the right proportion of cast iron to produce a steel with the desired carbon content.

789. The Bessemer process.   In the Bessemer process 20 or 30 tons of melted pig-iron are charged into a pear-shaped furnace known as a **converter,** while it is in a horizontal position (Fig. 144).   The bottom of the converter is filled with
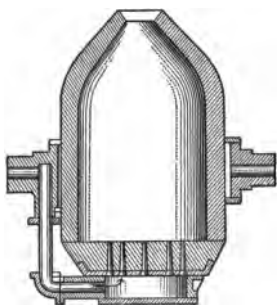
small holes through which a blast of air may be driven.   The blast is turned on and the converter revolved to an upright position.   The great rush of air passing through the iron burns out the silicon, manganese, and carbon. The operator in charge judges when the action is over by the nature of the flame issuing from the converter. The whole process takes from ten to twenty minutes.   The converter is then revolved to a horizontal position and a definite quantity of **spiegeleisen,** a very white iron rich in manganese and carbon, is added.   The amount of this iron added varies according to the amount of carbon wanted in the finished steel.   The manganese reduces any iron oxide formed during the "blow."

FIG. 144

790. Chemical properties.   Chemically pure iron is almost unknown.   All the iron with which we are familiar contains carbon, sulphur, silicon, phosphorus, and manganese.   Iron exposed to moist air rusts.   This rust is essentially ferric oxide, Fe_2O_3:

$$4 Fe + 3 O_2 = 2 Fe_2O_3.$$
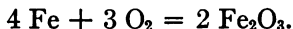
Fine iron wire, when once ignited, burns violently in pure oxygen forming **magnetic oxide,** Fe_3O_4.   This is a steel-blue solid having magnetic properties.   It is a mixture of ferrous oxide, FeO, with ferric oxide, Fe_2O_3.

Iron dissolves in dilute hydrochloric and sulphuric acids

with the liberation of hydrogen and formation of the corresponding ferrous salts:

$$Fe + 2\,HCl = FeCl_2 + H_2.$$
$$Fe + H_2SO_4 = FeSO_4 + H_2.$$
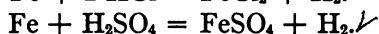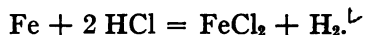
In these reactions the phosphorus and sulphur combine with some of the hydrogen and come out as the corresponding hydrogen compounds H_2S and PH_3, both of which gases have very disagreeable odors. Nitric acid dissolves iron with the formation of ferric nitrate and the liberation of oxides of nitrogen:

$$Fe + 4\,HNO_3 = Fe(NO_3)_3 + 2\,H_2O + NO.$$
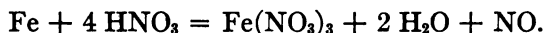
Iron combines directly with the halogens to form ferric salts, and with sulphur to form ferrous sulphide.

791. Reactions of ferrous salts. Solutions of ferrous salts give with ammonium hydroxide a white precipitate of ferrous hydroxide which rapidly turns brown; treated with a solution of potassium ferrocyanide a light-blue precipitate is produced. When a ferrous solution is treated with potassium ferricyanide, a deep-blue precipitate (**Turnbull's blue**) is formed.

A ferrous salt in solution may be changed to the ferric salt by treating it with some of the required acid and an oxidizing agent:

$$6\,FeCl_2 + 6\,HCl + 2\,HNO_3 = 6\,FeCl_3 + 4\,H_2O + 2\,NO.$$
$$10\,FeSO_4 + 2\,KMnO_4 + 8\,H_2SO_4 = 5\,Fe_2(SO_4)_3 + K_2SO_4 +$$
$$2\,MnSO_4 + 8\,H_2O.$$
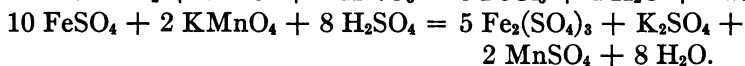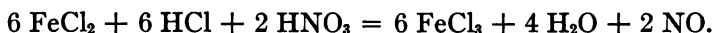
792. Reactions of ferric salts. Solutions of ferric salts give with ammonium hydroxide a brown gelatinous precipitate of **ferric hydroxide**; with ammonium thiocyanate a deep-red solution; with potassium ferrocyanide a deep-blue precipitate of **Prussian blue**; with potassium ferricyanide no precipitate is formed. Ferric solutions may be reduced to ferrous solutions by adding certain reducing agents. Hydrogen sulphide will change ferric chloride to ferrous chloride with the precipitation of sulphur:

$$2\,FeCl_3 + H_2S = 2\,FeCl_2 + 2\,HCl + S.$$
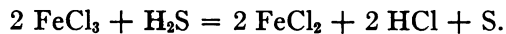
Stannous chloride will produce a similar reduction:

$$2\,FeCl_3 + SnCl_2 = 2\,FeCl_2 + SnCl_4.$$
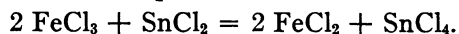
If sulphur dioxide be allowed to bubble through a ferric solution it will change the iron to the ferrous condition:

$$2 \text{ FeCl}_3 + 2 \text{ H}_2\text{O} + \text{SO}_2 = 2 \text{ FeCl}_2 + 2 \text{ HCl} + \text{H}_2\text{SO}_4.$$
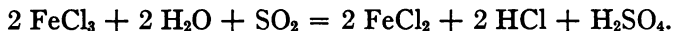
793. Test for ferrous and ferric iron. From the reactions described in the last two paragraphs it is apparent that potassium thiocyanate will give a red solution in the case of ferric iron, and nothing in the case of ferrous iron. Potassium ferricyanide gives a deep-blue precipitate in the case of ferrous solutions and nothing in the case of ferric.

794. Common compounds. Ferric oxide, Fe_2O_3; magnetic oxide, Fe_3O_4; ferrous chloride, $\text{FeCl}_2 \cdot 4 \text{ H}_2\text{O}$; ferric chloride, FeCl_3; ferrous sulphate, or green vitriol, $\text{FeSO}_4 \cdot 7 \text{ H}_2\text{O}$; ferrous sulphide, FeS; ferrous hydroxide, Fe(OH)_2; ferric hydroxide, Fe(OH)_3; ferrous iron alum, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6 \text{ H}_2\text{O}$; potassium ferrocyanide, yellow prussiate of potash, $\text{K}_4\text{Fe(CN)}_6$; potassium ferricyanide, red prussiate of potash, $\text{K}_3\text{Fe(CN)}_6$.

795. Ferric oxide, Fe_2O_3, occurs in nature as the iron ore **hæmatite.** Ground with clay it forms a cheap pigment used for painting roofs. **Indian red** is ferric oxide made by heating ferrous sulphate. **Venetian red** is a pigment made by heating ferrous sulphate with gypsum.

796. Ferrous sulphate, green vitriol, or copperas, $\text{FeSO}_4 \cdot 7 \text{ H}_2\text{O}$. This salt may be made by dissolving iron in dilute sulphuric acid and crystallizing the product. It is used as a mordant in dyeing, in the preparation of ink, as a disinfectant, in the manufacture of Prussian blue and other pigments, and for the preparation of fuming sulphuric acid.

797. Ferric chloride, FeCl_3. This compound may be formed by the direct union of chlorine with iron, by passing a stream of chlorine into a solution of ferrous chloride, or by dissolving ferric oxide in hydrochloric acid (**250**). It crystallizes from solution with 6 molecules of water of crystallization in minute yellow deliquescent crystals. Its water solution reacts strongly acid.

798. Ferrous ammonium sulphate, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6 \text{ H}_2\text{O}$. This is a beautiful green crystalline salt made by crystallizing equal molecular weights of ferrous sulphate and ammonium

sulphate from water solution. It does not change in air and is much used in analysis as a standardizing material.

799. Blue-print paper. When potassium ferricyanide is added to a ferric solution no precipitate or blue color is formed. Blue-print paper may be made by covering one side of a piece of paper with a solution of a mixture of a ferric salt with potassium ferricyanide. This should be done in a dark room and the paper allowed to dry without being exposed to light. When the paper is exposed to daylight some of the ferric salt is reduced to the ferrous condition. After this, if the paper be moistened, the ferrous salt reacts with the ferricyanide and produces a deep-blue color, Turnbull's blue. Portions not exposed to the light will show no color after the washing.

CHAPTER XLVIII

Aluminum and Chromium

Aluminum (Laboratory Exercise No. 36)

800. Appearance and occurrence. Aluminum is a light, white metal. It does not occur in the free condition, although abundant in compounds. It is estimated that about 7 per cent of the weight of the earth is aluminum. It is a constituent of **cryolite**, Na_3AlF_6; **feldspar**, $KAlSi_3O_8$; mica, $H_2KAl_3(SiO_4)_3$; **bauxite**, $Al_2O_3 \cdot 2\ H_2O$; **corundum, ruby,** and **sapphire** are different forms of aluminum oxide. **Clay** is formed by the decomposition of granite and feldspar.

801. Physical properties. Aluminum has a specific gravity of 2.6. It is tough, malleable, and ductile, and can be rolled out into thin sheets and drawn out into wire. It melts at 657° and boils at about 1600°. It is a good conductor of electricity.

802. Chemical properties. At a high temperature aluminum burns to the oxide, Al_2O_3, with the evolution of a great amount of heat.

Toward strong acids this oxide is basic, but toward strong bases it is acidic:

$$Al_2O_3 + 3\ H_2SO_4 = Al_2(SO_4)_3 + 3\ H_2O.$$
$$Al_2O_3 + 6\ NaOH = 2\ Na_3AlO_3 + 3\ H_2O.$$
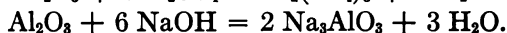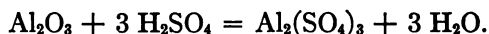
The metal is almost insoluble in nitric acid, but dissolves readily in hydrochloric acid and in solutions of the alkalies with the evolution of hydrogen:

$$2\ Al + 6\ HCl = 2\ AlCl_3 + 3\ H_2.$$
$$2\ Al + 6\ NaOH = 2\ Na_3AlO_3 + 3\ H_2.$$
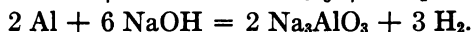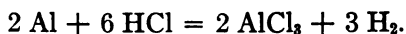
Ammonium hydroxide added to a solution of an aluminum salt gives a gelatinous precipitate of **aluminum hydroxide**. This compound is basic toward strong acids but acidic toward strong

448

bases. As a base its formula is $Al(OH)_3$; as an acid its formula might be written H_3AlO_3:

$$Al(OH)_3 + 3\,HCl = AlCl_3 + 3\,HOH.$$
$$H_3AlO_3 + 3\,NaOH = Na_3AlO_3 + 3\,HOH.$$
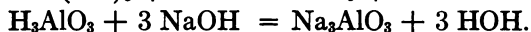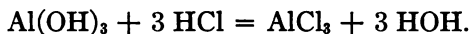
The metal itself is a powerful reducing agent. If the finely divided metal be mixed in molecular proportions with metallic oxides and the mixture ignited, a violent reaction takes place with the evolution of great heat. The aluminum combines with the oxygen of the oxide and the other metal is set free:

$$Fe_2O_3 + 2\,Al = Al_2O_3 + 2\,Fe.$$
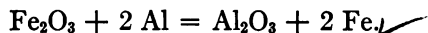
803. Test. If ammonium hydroxide be added to a solution of an aluminum salt, a colorless gelatinous precipitate of aluminum hydroxide will be formed. This precipitate will remain after boiling. Ammonium carbonate and ammonium sulphide also precipitate the hydroxide (**250**).

804. Preparation. Aluminum was formerly made by the action of metallic sodium on aluminum chloride:

$$AlCl_3 + 3\,Na = 3\,NaCl + Al.$$
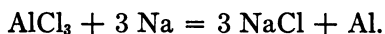
This process has now entirely given place to **Hall's process,** in which aluminum oxide, dissolved in molten cryolite, is electrolyzed. The process is carried out in a large iron cell (Fig. 145), lined with carbon. The carbon lining constitutes the negative electrode. The positive electrode consists of a large number of rods of carbon suspended in the cell. Cryolite is first added to the cell and melted. Powdered aluminum oxide is then thrown in and dissolves at once in the cryolite. As the electrolysis proceeds, the aluminum oxide only is de-
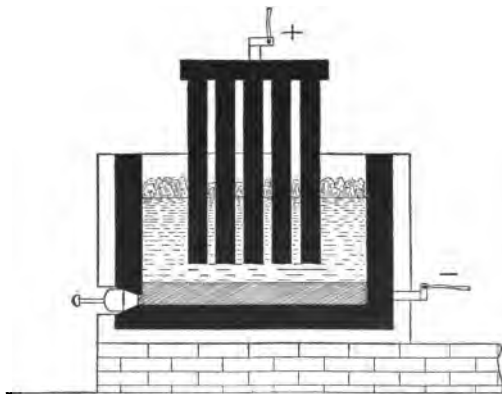
FIG. 145

composed, the aluminum settling in the bottom of the cell. The cryolite remains unchanged. More of the oxide is added from time to time when necessary.

805. Uses. The metal is used in the manufacture of iron and steel, for cooking utensils, and for electric cables. It is also used in many alloys. **Aluminum bronze** contains 90 per cent copper and 10 per cent aluminum. **Magnalium** metal contains 70 per cent to 90 per cent aluminum and the rest magnesium. This metal is very light and takes a high polish.

806. The Thermite process. In this process metallic oxides are reduced by means of aluminum. The reaction is accompanied by a great evolution of heat and the reduced metal is left in a very liquid condition. The process is of great use in mending every known kind of break in iron or steel machinery parts. By means of it it is possible to produce melted iron in any place or position. A mould is formed over the fracture. A crucible (Fig. 146) containing a mixture of iron oxide and aluminum is arranged over the mould and the mixture ignited. The melted iron is allowed to flow into the break where it melts the adjacent parts and forms a perfect weld. (Fig. 147 shows the iron being run into the mould and Fig. 148 shows the work after the removal of the moulding sand.) The process is also convenient for preparing some metals which cannot be easily prepared in any other way, such as manganese, chromium, and molybdenum.
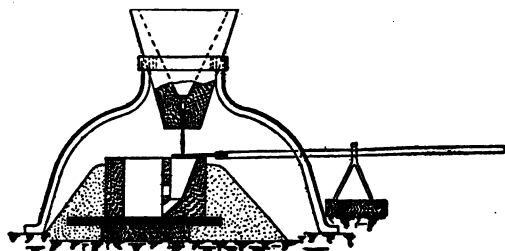
FIG. 146

807. Compounds. Aluminum oxide, Al_2O_3; **aluminum chloride,** $AlCl_3 \cdot 6 H_2O$; **aluminum sulphate,** $Al_2(SO_4)_3 \cdot 18 H_2O$; **alum,** $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24 H_2O$; aluminum acetate, $Al(C_2H_3O_2)_3$.

808. Aluminum oxide, alumina, Al_2O_3. This material occurs in nature as **corundum.** An impure form known as **emery** is used as an abrasive. **Ruby** is pure aluminum oxide colored
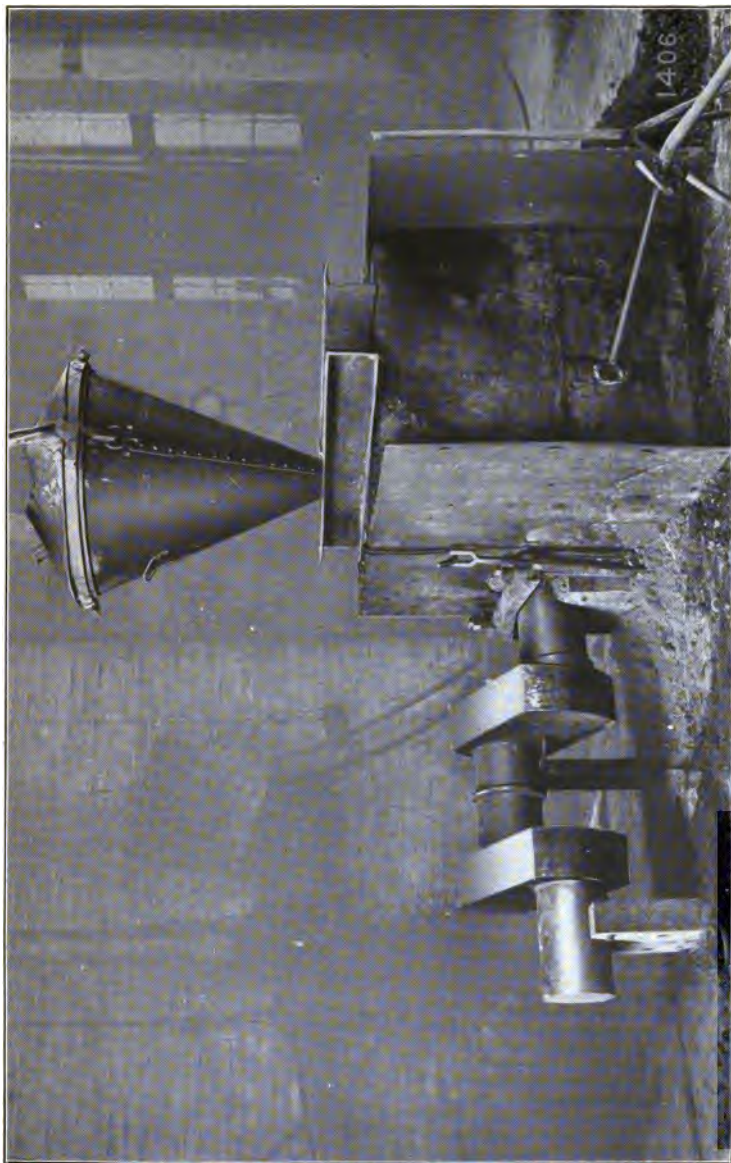
Courtesy of the Goldschmidt Thermit Company

Fig. 147. Mould-Box and Crucible in Position During the Preheating Operation

Fig. 148. Thermit Weld, Showing Pouring-Gate and Riser

by a trace of chromium. Aluminum oxide may be prepared by heating aluminum hydroxide or by reducing a metallic oxide with aluminum.

809. Aluminum hydroxide, $Al(OH)_3$. This is a colorless gelatinous precipitate, formed when ammonium hydroxide is added to a solution of an aluminum salt. When aluminum hydroxide is precipitated in a solution containing finely divided matter in suspension it carries the suspended matter down with it as a precipitate, leaving the solution clear. This principle is made use of in the clarification of water for drinking purposes. For this purpose some aluminum salt is added to the water. It is hydrolyzed by the water and aluminum hydroxide formed (**250**). This settles to the bottom of the reservoir and carries all suspended matter with it.

810. Lakes. If aluminum hydroxide be precipitated in a solution colored with an organic dye or coloring matter, all of the color combines with the hydroxide and is carried down with the precipitate. Pigments formed by drying and grinding this precipitate are known as **lakes.**

811. Mordants. Mordants are substances used in dyeing to cause the color to adhere firmly to the fibres of the cloth. Substances like the hydroxides of aluminum, iron, chromium, and tin will not only adhere to the fibres of cloth but will also form lakes with coloring matter. If a piece of cloth be first soaked in a solution of a salt of one of the above metals and then boiled in water colored with a dye, the color adheres firmly to the fibres.

812. Alums. An alum is a double sulphate of a trivalent metal with an alkali sulphate. Common alum is formed from aluminum sulphate and potassium sulphate. Alums contain 24 molecules of water of crystallization, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\ H_2O$. Other common alums are ferric ammonium alum, $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24\ H_2O$; ammonium aluminum alum, $(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\ H_2O$; and chrome alum, $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24\ H_2O$.

Chromium

813. Appearance and occurrence. Chromium is a very hard, steel-gray metal. It does not occur in the free condition, but is found as **chromite, $Fe(CrO_2)_2$.**

814. Properties. The metal is fusible with great difficulty, melting at a temperature above 1500°. It forms several oxides: **chromous oxide, CrO; chromic oxide, chrome green, Cr_2O_3,** and **chromium trioxide, CrO_3.** The first two oxides are basic, while the trioxide is acidic. Chromous oxide with water forms chromous hydroxide, which is basic and gives rise to the formation of chromous salts. Chromic oxide with water forms chromic hydroxide, which reacts both basic and acidic. With a strong acid it forms chromic salts, while with strong bases it forms chromites:

$$2\ Cr(OH)_3 + 3\ H_2SO_4 = Cr_2(SO_4)_3 + 6\ HOH.$$
$$H_3CrO_3 + NaOH = NaCrO_2 + 2\ H_2O.$$
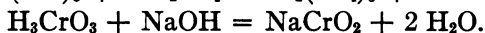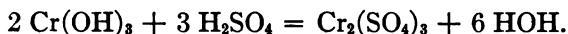
Like aluminum hydroxide, chromic hydroxide is precipitated when an alkali hydroxide, carbonate, or sulphide is added to a solution of a chromic salt. The precipitate is green in color and gelatinous.

815. Preparation. Chromium is most readily prepared by reducing chromic oxide with aluminum. The reaction when once started proceeds with an enormous evolution of heat. The melted metal settles to the bottom of the crucible. The aluminum oxide formed settles in a liquid layer on top of the chromium.

816. Uses. Metallic chromium is used in the manufacture of special chrome steels much used in automobile bearings. Compounds of chromium are used as paint pigments and as oxidizing agents.

817. Compounds. Chromic oxide, Cr_2O_3; chromic hydroxide, $Cr(OH)_3$; chromium trioxide, CrO_3; potassium chromate, K_2CrO_4; potassium dichromate, $K_2Cr_2O_7$; lead chromate, $PbCrO_4$; chrome alum, $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24\ H_2O$.

818. Chromium trioxide, chromic anhydride, CrO_3. Chromium trioxide is a red crystalline solid formed when a saturated solution of potassium dichromate in concentrated sulphuric acid

is allowed to stand. Although it is an oxide of a metal, it is the anhydride of chromic and dichromic acids:

$$CrO_3 + H_2O = H_2CrO_4.$$
$$2 CrO_3 + H_2O = H_2Cr_2O_7.$$

It is a powerful oxidizing agent, liberating chlorine from hydrochloric acid instantly:

$$2 CrO_3 + 12 HCl = 2 CrCl_3 + 3 Cl_2 + 6 H_2O.$$

819. Chromates and dichromates. Potassium chromate is a bright-yellow crystalline salt, K_2CrO_4. It is a powerful oxidizing agent as shown by the equation:

$$2 K_2CrO_4 = 2 K_2O + Cr_2O_3 + 3 O.$$

When added to a solution of a lead salt it forms a precipitate of lead chromate (**chrome yellow**):

$$K_2CrO_4 + Pb(NO_3)_2 = \underline{PbCrO_4} + 2 KNO_3.$$
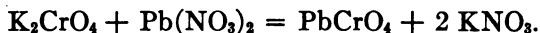
When a strong solution of potassium chromate is treated with an acid, the color turns red, due to the formation of the dichromate ion:

$$2 K_2CrO_4 + H_2SO_4 \rightleftharpoons K_2SO_4 + K_2Cr_2O_7 + H_2O.$$

Potassium dichromate is a beautiful red crystalline salt formed when 1 molecular weight of chromium trioxide is added to a solution of potassium chromate:

$$K_2CrO_4 + CrO_3 \rightleftharpoons K_2Cr_2O_7.$$

From this it is apparent that the dichromate is nothing but the normal chromate with one extra acid anhydride. It is sometimes called acid potassium chromate. With water it reacts acid. When added to a solution of lead nitrate it gives a precipitate of lead chromate:

$$K_2Cr_2O_7 + H_2O = H_2CrO_4 + K_2CrO_4.$$
$$K_2CrO_4 + Pb(NO_3)_2 = PbCrO_4 + 2 KNO_3.$$
$$\underline{H_2CrO_4 + Pb(NO_3)_2 = PbCrO_4 + 2 HNO_3.}$$
$$H_2O + K_2Cr_2O_7 + 2 Pb(NO_3)_2 = 2 PbCrO_4 + 2 KNO_3 + 2 HNO_3.$$
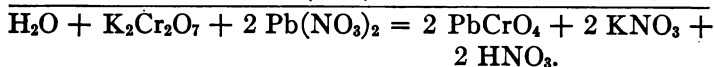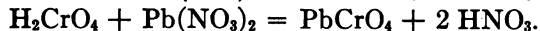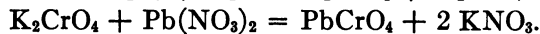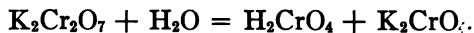
Potassium dichromate is even a more powerful oxidizing agent than the chromate:

$$K_2Cr_2O_7 = K_2O + Cr_2O_3 + 3 O.$$
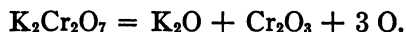
The oxidation is usually carried out in the presence of sulphuric acid, which combines with the basic oxides, forming sulphates.

When a chromate or a dichromate is used as an oxidizing agent the color changes from yellow or red to a green.

If a solution of potassium hydroxide be added to a solution of a dichromate, it is changed to the normal chromate:

$$K_2Cr_2O_7 + 2\ KOH = 2\ K_2CrO_4 + H_2O.$$
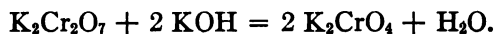
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